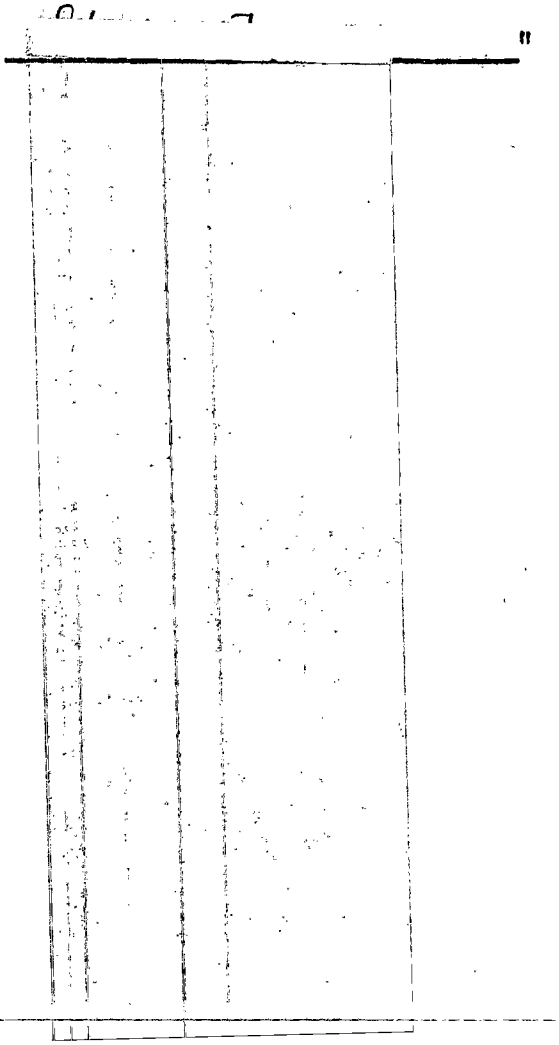
"In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.



SOME STUDIES ON THE HALIDES OF METHANE

PART I
THE EFFECT OF HALOGEN ATOMS UPON THE S_N2 REACTIVITY OF OTHER HALOGEN ATOMS ATTACHED TO THE SAME CARBON ATOM

PART II
AN EMPIRICAL METHOD FOR PREDICTION OF THE BOILING POINTS OF THE HALOMETHANES

PART III
A CORRELATION OF REACTIVITIES IN THE BASIC SOLVOLYSIS OF HALOFORMS

A THESIS

Presented to
the Faculty of the Graduate Division

By

Stanton Jay Ehrenson

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

Georgia Institute of Technology
June 1957

5-8
12T

SOME STUDIES ON THE HALIDES OF METHANE

PART I
THE EFFECT OF HALOGEN ATOMS
UPON THE S_N2 REACTIVITY OF OTHER
HALOGEN ATOMS ATTACHED TO THE SAME CARBON ATOM

PART II
AN EMPIRICAL METHOD FOR PREDICTION
OF THE BOILING POINTS OF THE HALOMETHANES

PART III
A CORRELATION OF REACTIVITIES
IN THE BASIC SOLVOLYSIS OF HALOFORMS

Approved:

Date approved by Chairman: February 13, 1957

ACKNOWLEDGEMENTS

My sincerest thanks are to be expressed initially to Dr. Jack Hine whose continued interest and guidance served as invaluable and stimulating aids during the course of this investigation. To the National Science Foundation, the Tennessee Eastman Corporation and the Office of Ordnance Research my gratitude is also due for the grants that supported the work. I am likewise appreciative of the time and helpful information concerning use of the electronic computer provided by Drs. W. F. Atchison and J. C. Currie.

TABLE OF CONTENTS

PART III

LIST OF TABLES

PART I

PART II

PART III

LIST OF ILLUSTRATIONS

PART I

PART II

SUMMARY

Part I

Information on the effects of halogen substitution for hydrogen in the methyl halides had previously been obtained by kinetic studies of the S_N2 reactions with methoxide ion in methanol and iodide ion in acetone. While the deactivation effects of the halogens as substituents were qualitatively similar for the reactions with both these nucleophiles, differences in magnitude were evident. In order to provide a wider perspective on the subject and in an attempt to uncover the reasons for the quantitative differences noted, the reactions of the methylene halides with the strongly nucleophilic thiophenolate ion in methanol were studied.

All the methylene halides examined with the exception of those containing fluorine react by the mechanism

$$C_6H_5S^- + CH_2XY \xrightarrow{k_1} C_6H_5SCH_2Y + X^-$$

$$C_6H_5S^- + C_6H_5SCH_2Y \xrightarrow{k_2} (C_6H_5S)_2CH_2 + Y^-$$

with $k_2 \gg k_1$. The fluoromethyl halides undergo the initial displacement; the resulting fluoromethyl phenyl thioether is resistant to further attack. Experimentally following the reactions by titration of the unreacted thiophenol with standard methanolic iodine allowed calculation of the rate constants (k_1) and the heats and entropies of activation that appear in Table 1.

Table 1. Kinetic Constants for Reactions of Methylene Halides with Sodium Thiophenolate in Methanol

Halide	$10^4 k_1$ (l./m.s.) 0.0°	40°	ΔHa Kcal.	ΔSa e.u.
ICH_2I [1]	1.19 ± .01	108 ± 2	18.6 ± 0.1	-8.5 ± 0.4
$BrCH_2I$	0.811 ± .018	79.8 ± 1.6	18.9 ± 0.2	-7.9 ± 0.6
$ClCH_2I$	1.83 ± .03	149 ± 3	18.1 ± 0.2	-9.2 ± 0.7
FCH_2I	47.9 ± .9	964 ± 20 [2]	15.9 ± 0.2	-10.8 ± 0.8
$BrCH_2Br$ [1]	.0798 ± .0004	10.0 ± .2	20.0 ± 0.2	-8.7 ± 0.5
$ClCH_2Br$	.228 ± .002	25.1 ± .3	19.4 ± 0.1	-8.6 ± 0.3
FCH_2Br	1.88 ± .03	152 ± 5	18.1 ± 0.2	-9.2 ± 0.8
$ClCH_2Cl$ [1]	.0214 ± .0010 [3]	.222 ± .007	21.1 ± 0.7	-12.5 ± 2.6

[1] Rate constants contain a statistical factor of one-half.

[2] At 30°C.

[3] At 20.35°C.

Consistent with the data obtained from the reactions with iodide and methoxide, the alpha substituent halogens are seen to deactivate halide displacement by thiophenolate in the order

$$Br > I > Cl > F$$

The deactivation effects in the reactions with thiophenolate are found to exhibit greater quantitative similarity to those with iodide than with methoxide ion. This observation seems reasonable; thiophenolate

and iodide ions are strong and relatively large nucleophiles while methoxide is weaker and smaller.

In pursuing the matter further, it appears that the overall deactivations are not resolvable solely in terms of steric hindrance and an inductive effect. While both should contribute to deactivation, the differences in effects between substituent halogens do not agree with expectations based on van der Waal radii and electronegativity values (taken as rough measures of the steric and inductive contributions respectively). The large effect accompanying substitution of chlorine for fluorine compared to that for bromine for chlorine substitution is discussed in terms of the additional factor of activation by strong π bonding (electron donation) by substituent fluorine. The steric and two electronic factors (induction and π bonding) are employed in combination to rationalize the other effects noted in the thiophenolate and iodide ion reactions. Some of the physical (bond lengths, electronegativities, etc.) and reactivity properties of the methylene halides and related compounds are employed in an attempt to gage the relative contributions of the separate effects. The methoxide reactions are discussed in similar terms. To account for the small deactivation effect of fluorine as substituent the additional factor of π bonding by methoxide in the transition state is suggested.

Reexamination of the reaction system, ethyl bromide, iodide ion in acetone was undertaken; previous studies had yielded falling rate constants. The kinetic constants obtained also fell with no ascertainable explanation. A rate value was estimated at twenty degrees ($k = 120 \times 10^{-5}$ l./m.s.) by extrapolation and found to be substantially in agreement with the results obtained by other investigators.

Part II

A correlation has been formulated between the normal boiling points of the related group of compounds comprising the halides of methane with two of the observable features of the particular compounds, namely the number and type of halogen contained. The results of this study may be applied to predict the boiling point values of halomethanes as yet unexamined.

The difference in boiling points (D) between the particular halide of methane and methane is expressed as an empirical linear function of parameters for the halogens contained and a structure parameter in the following general form:

$$D = n_F X_F + n_{Cl} X_{Cl} + n_{Br} X_{Br} + n_I X_I + X_{CH_n}$$

where the particular n_{Hal} value is the number of each halogen present and the X values are the parameter coefficients to be determined. It was ascertained that this equation would satisfactorily fit, with respect to minimization of the error of fitting, all 69 of the halides of methane with the four X_{Hal} and three X_{CH} parameters. Of the latter, those for the methyl, methylene and haloform structures were chosen, that for the tetrahalomethanes was taken as zero.

Employing data obtained from the literature on 46 compounds, of which 16 were considered particularly reliable and therefore doubly weighted, the seven coefficients were determined by a least squares treatment run on an electronic computer. The values obtained are

$X_F = 7.15$ $X_{CH_3} = 77.68$

$X_{Cl} = 59.06$ $X_{CH_2} = 85.99$

$X_{Br} = 87.15$ $X_{CH} = 46.79$

$X_I = 125.02$

For all of the 46 compounds employed in the correlation, the predicted and observed boiling points differ by an average of 2.4 degrees (standard deviation, 3.4 degrees). For the 16 reliable compounds, the average and standard deviations were respectively 1.7 and 2.0 degrees. For six other compounds (not employed in the correlation) whose boiling points were observed at lower temperatures or were accompanied by decomposition, the predicted values agreed with those obtained by extrapolation to one atmosphere pressure within an average of 4.5 degrees.

In light of the empirical nature of this treatment, it was of interest to note that the parameter coefficient values for the halogens are expressible as a linear function of the boiling points of the corresponding halogen diatomic molecules:

$$X_{Hal} = 0.317\ B.P._{Hal}\ (°K.) - 18.5°.$$

Part III

Previous investigations have established that the basic hydrolysis reactions of many of the haloforms proceed by the alpha elimination mechanism

$$CHX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{k_2} CX_2 + X^- \qquad \text{(rate determining)}$$

$$CX_2 \xrightarrow{OH^-,\ H_2O} CO + HCO_2^-$$

It was felt that if the reactivities of the haloforms could be related to their structures through consideration of the mechanism of reaction, increased confidence in the applicability of the mechanism would be provided. Also a means of prediction of the hydrolysis rates of the haloforms as yet unexamined and some idea of how the particular halogens contribute to the relative reactivities would be obtained.

Recognizing that the decomposition of the trihalocarbanion to the dihalomethylene and halide ion constitutes the rate controlling step, a semi-empirical linear free energy expression was developed, equating parameters for the halogens lost as the anion and those retained in the dihalomethylene to the rate constant k_2 and thence to the observable rate constants k_h and k_1. The employed form of the correlation equation is

$$\log \frac{\left(\frac{k_h}{k_1 - k_h}\right)_{CHXYZ}}{\left(\frac{k_h}{k_1 - k_h}\right)_{CHCl_3}} = \sum_{X,Y} M + N_Z + \log\left(\frac{n}{3}\right) + (c) \log\left(\frac{k_1^{CHXYZ}}{k_1^{CHCl_3}}\right)$$

where the M values are the dihalomethylene stabilization factors for the halogens, N_Z is the parameter for the halogen lost as the anion in the rate determining step, n is the number of halogens of type Z and c is a constant. Since the correlation is one of relative reactivities,

reference is made to chloroform and the $\underline{M}$ and $\underline{N}$ values for chlorine are therefore taken as zero.

The hydrolysis and proton removal rates for several of the haloforms were available and preliminary calculations suggested that an equation of this type might provide a satisfactory correlation. To determine the numerical parameter values however, the hydrolysis rates of additional haloforms were necessary. Following the reactions by titration of the unreacted base with standard acid allowed calculation of the rate constants for hydrolysis that appear in Table 2. In conjunction with the data available on the other haloforms the correlation calculations were made by a method of trial and error to obtain the best fit. The rate constants at zero degrees (several by extrapolation) for ten haloforms were correlated with the following results:

$$M_F = 3.95 \qquad N_{Br} = 0.65$$
$$M_{Br} = -1.60 \qquad N_I = -0.10$$
$$M_I = -2.80 \qquad c = 0.5$$

Employing these parameter values, the k_h values of the nine haloforms (besides chloroform) used in the correlation, fitted with less than 10 per cent deviations on the average. Interpretation of these values indicates that bromide and iodide ions are lost in the rate determining step respectively about five times as, and slightly less, readily than chloride ion (from the $\underline{N}$ values), and that the order of dihalomethylene stabilization is

$$F > Cl > Br > I$$

from the M values. The positive c value suggests that the trihalocarbanions lose more carbanion character in the transition state of their transformation to haloform than they do in the transition state to the dihalomethylene.

A similar treatment of the basic solvolysis rates in two-thirds dioxane and methanol was undertaken, with the difference that the relative rates of proton removal from the haloforms (k_1) were estimated by a method shown to hold in water and assumed to apply in these solvents. The rate constants for solvolysis which were obtained in a manner similar to those for reactions in pure water appear in Tables 2 and 3. Sufficient data were collected to show that chlorine, bromine containing haloforms are well fit by the correlation method in the dioxane solvent, but not in methanol. The chlorine, iodine compounds in dioxane also exhibit some deviation. Because of the possibility of competing side reactions, e.g., oxidation, which may obscure the solvolyses, re-runs of some of the reactions, notably bromoform in methanol and iodoform in dioxane, should precede acceptance of these deviation-exhibiting-systems as detractions from the generality of the method.

Studies were also conducted on the rates of hydrolysis of three of the haloforms over a wide range of aqueous dioxane mixtures (see Table 3). The results suggest that the solvent effects are quite complicated, possibly involving ion pair formation as the dielectric value of the solvent medium is decreased.

Table 2. Haloform Hydrolysis Rates in Water (W), Two-Thirds Aqueous Dioxane (D) and Rates of Methanolysis (M)

Compound		10^4k (l./m.s.) 25°	50°
$CHCl_3$	(M)		0.306 ± 0.004
$CHCl_2Br$	(W)		307 ± 24
	(M)		9.25 ± 0.05
$CHClBr_2$	(W)		220 ± 13
	(M)		6.30 ± 0.07
$CHBr_3$	(W)[1]	1.99 ± 0.03	83.8 ± 3.4
$CHCl_2I$	(W)	2.17 ± 0.03	95.2 ± 5.8
$CHClI_2$	(W)	112 ± 25 [2]	9.21 ± 0.29
	(D)	179 ± 9 [2]	17.7 ± 0.3

[1] At 35°C., 10^4k = 9.54 ± 0.14

[2] At 67.1°C.

Table 3. Haloform Hydrolysis Rates in Aqueous Dioxane at 35°C.

Compound	10^4k (l./m.s.) (Volume Per Cent Dioxane)
$CHCl_3$	3.00 ± 0.04 (19.6), 3.48 ± 0.05 (49), 3.42 ± 0.07 (60), 3.01 ± 0.03 (66.7), 3.45 ± 0.06 (72), 4.24 ± 0.08 (78.4),
$CHCl_2Br$	65.6 ± 0.8 (29.4), 70.6 ± 1.1 (40), 80.7 ± 1.3 (50), 76.8 ± 1.2 (60), 83.8 ± 1.2 (66.7), 86.0 ± 0.7 (75),
$CHBr_3$	11.0 ± 0.1 (36.4), 11.6 ± 0.1 (50), 12.1 ± 0.1 (66.7)

PART I

THE EFFECT OF HALOGEN ATOMS UPON THE S_N2 REACTIVITY OF OTHER HALOGEN ATOMS ATTACHED TO THE SAME CARBON ATOM

CHAPTER I

INTRODUCTION

The effects upon S_N2 displacement[1] of a given group from carbon exercised by substituents located upon the same carbon atom have been the object of considerable attention. Specifically of interest in the studies to be described are the cases where both the displaced group and substituent are halogens. The methylene halides have been studied quantitatively in the solvent acetone with iodide ion and in methanol with methoxide ion (1). In agreement with the conclusions drawn by Petrenko-Kritschenko from semi-quantitative investigations on several organic polyhalides (2) and other fragmentary studies described briefly in reference (1), the substitution of any halogen for an alpha hydrogen was found to decrease the S_N2 reactivity.

In both acetone-iodide and methanol-methoxide media the reactivity of the methyl halides varied with alpha substitution in the following order.

$$H > F > Cl > Br \sim I$$

In reactions toward methoxide the deactivation order of substituent bromine relative to iodine is impossible to estimate because of the similar reactivities of bromides and iodides. Toward iodide ion, bromine is a

---

[1] For a thorough discussion of the significance of the term S_N2 see C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

(1) J. Hine, C. H. Thomas and S. J. Ehrenson, J. Am. Chem. Soc., 77, 3886 (1955).

(2) P. Petrenko-Kritschenko, V. Opotsky, M. Diakowa and A. Losowog, Ber., 62B, 581 (1929).

better deactivator than iodine. In the reactions where bromide is displaced by methoxide, the reactivity is decreased more by methyl than by fluorine substitution. Fluorine is the stronger deactivator, however, towards iodide in acetone, a comparison complicated by reversibility and alkali halide precipitation in the ethyl bromide reaction (3).

It seemed desirable therefore to study the reactivities of the methylene halides toward another nucleophile prior to any serious attempt to explain the effects of alpha substitution.

The thiophenolate ion was chosed primarily because of its strong nucleophilicity and preliminary information, gained in this laboratory, indicating sizable differences in the rates of bromide and iodide displacement. In going from methoxide in methanol to thiophenolate in the same solvent the ratio of iodide to bromide displacement rate for the alpha chloro substituted compound was increased by about threefold. The overall efficacy of thiophenolate as a nucleophile had previously been demonstrated in reactions with polymethylene dihalides (4).

Description of the techniques employed and results obtained from the thiophenolate-methylene halide-methanol system have recently been published (5). A more comprehensive coverage follows. Included as well are details of a reinvestigation of the reaction of iodide ion with ethyl bromide in acetone.

---

(3) I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 161 (1946).

(4) W. H. Brader, Jr., Ph.D. Thesis, Georgia Institute of Technology, 1954.

(5) J. Hine, S. J. Ehrenson, and W. H. Brader, Jr., J. Am. Chem. Soc., 78, 2282 (1956).

CHAPTER II

PROCEDURE

Experimental

Kinetics of the $C_6H_5SNa + CH_2XY$ Reactions.--The sensitivity of thiophenolate ion to oxidation (6) precluded preparation of stock solutions. Standard solutions were prepared by weighing thiophenol into a volumetric flask under nitrogen[1] and, preliminary to dilution with absolute methanol, adding about a two per cent excess of sodium methoxide. The dihalides were also weighed into volumetric flasks and diluted either to the mark or with a pipetted volume of methanol. The latter procedure was employed with methylene fluorobromide and chloride. To avoid volatility losses, separate samples of these dihalides were weighed into 50 ml. volumetrics containing 20 ml. methanol. The volumetric flasks that served as the reaction vessels were thermostatted and standard thiophenolate added. In the more general method, aliquots of both the halide and thiophenolate solutions, thermostatted to reaction temperature, were pipetted, in the order given, into erlenmeyer flasks immersed in the thermostatting bath.

For reaction temperatures other than zero degrees, a constant temperature (± 0.05°C.) water bath, containing black ink or dye and thereby essentially opaque, was employed. Zero degree runs were conducted in an

---

[1] All reactions as well as preparations were carried out under a nitrogen atmosphere.

(6) J. Xan, E. A. Wilson, L. D. Roberts and N. H. Horton, ibid., 63, 1139 (1941).

air-insulated, covered bath containing 18 liters of water-ice slurry. The temperature was found to remain at 0.0 to 0.1°C.

Reaction time was measured (on a stop watch in units of a quarter minute) from delivery of half the volume of thiophenolate solution into the reaction flask, to delivery of half the aliquot volume of the reaction solution into glacial acetic acid, employed to convert thiophenolate to unreactive thiophenol. The volatile dihalide reactions were stopped by addition of the acid to the reaction vessel. Vigorous shaking, following each addition, insured thorough mixing.

Titration of the unreacted thiophenol with standard $KI \cdot I_2$ in water (7) was unsatisfactory in that the end point was indistinct. Within about five per cent before the true end-point, an iodine color, which slowly faded, was noted. Whether water changes the redox potential for iodine and thiophenolate or complicates the titration in some other way is open to speculation; when standard methanolic iodine was found to yield sharp end points it was employed thereafter in all thiophenol titrations.

Kinetics of the C_2H_5Br + KI Reaction.--The rate constants calculated by Thomas (8) from the second order rate equation for the ethyl bromide, sodium iodide reaction in acetone at 20.3°C. fell sharply as the reaction proceeded. Runs at zero and twenty degrees were conducted with potassium iodide to provide independent checks upon the data and conclusions found in references (3) and (8).

Potassium iodide and ethyl bromide were weighed into volumetric flasks and diluted to the mark at the temperature of reaction with acetone.

---

(7) P. Klason and T. Carlson, Ber., 39, 738 (1906).

(8) C. H. Thomas, Ph.D. Thesis, Georgia Institute of Technology, 1953.

Aliquot samples (total volume 25 ml.) were withdrawn and mixed in thermostatted low actinic volumetric flasks. The reaction was stopped by addition of about ten grams of ice and timed as previously described. Titration of the unreacted iodide ion with standard iodate solution followed the method of Andrews (9) as modified by Conant and Kirner (10) and Thomas (8).

Runs at twenty degrees were thermostatted in the water bath described previously. Water at five degrees from a refrigerating unit was circulated through the bath coils in opposition to the heaters. The runs at zero degrees were thermostatted in a large (2 liter) Dewar flask containing water-ice slurry, and kept in a refrigerator except when samples were withdrawn.

Preparation and Purification of Reagents

Thiophenol.--Matheson Company thiophenol was used without purification. Titration with standard iodine indicated unoxidizable impurity at less than one per cent.

Sodium Methoxide.--Freshly cut sodium, washed in methanol, was added to absolute methanol in a polythene bottle. The reaction was carried out under nitrogen with cooling. Standardization, in aqueous solution against hydrochloric acid with phenolphthalein as indicator, preceded storing under nitrogen.

Methanol.--Commercial methanol was purified by the method of Fieser (11) and stored under nitrogen.

---

(9) L. W. Andrews, J. Am. Chem. Soc., 25, 756 (1903).

(10) J. B. Conant and W. R. Kirner, ibid., 46, 232 (1924).

(11) L. F. Fieser, Experiments in Organic Chemistry, Part II, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 359.

Methylene Chlorobromide.--Dow Company methylene chlorobromide was distilled and the fraction boiling at 68.8-69.2°C. (n_D^{24} 1.4812) was stored in a brown bottle under nitrogen.

Methylene Bromide.--The distilled fraction of Dow Company methylene bromide boiling at 97.4°C. (n_D^{25} 1.5384) was collected and stored in the same manner as the chlorobromide.

Methylene Iodide.--Eastman Kodak White Label methylene iodide was washed with sodium thiosulfate and several portions of distilled water, and stored over silica gel under nitrogen in a brown bottle.

Methylene Chloride.--Matheson methylene chloride was distilled through a Todd column. The fraction boiling at 40.0°C. was collected and stored in the usual manner.

Methylene Chloroiodide.--A sample of methylene chloroiodide (n_D^{24} 1.5817) prepared by Dr. W. H. Brader was employed without purification.

Methylene Bromoiodide.--Methylene bromoiodide was prepared by reacting 34.9 grams of sodium iodide with 30 ml. of methylene bromide in 200 ml. of acetone at 40°C. for twenty hours in the dark. Aspiration to remove about half the acetone from the dark brown reaction mixture was followed by three washings with aqueous sodium thiosulfate and one with water. The organic layer was dried with calcium chloride and distilled from under nitrogen. Fractions containing acetone (56°C.) and methylene bromide (94°C.) preceded the methylene bromoiodide which boiled at 132°C. at 748 mm. (n_D^{24} 1.6356). The product which was pink was stored in the conventional manner.

Methylene Fluorobromide.--The method of Haszeldine (12), modified as follows, was used to prepare methylene fluorobromide. To 67 grams of vacuum

---

(12) R. N. Haszeldine, J. Chem. Soc., 4259 (1952).

dried silver fluoroacetate suspended in 100 ml. of carbon tetrachloride (in a three-neck, 500 ml. round bottom flask) was added slowly, with stirring and heating an excess of bromine. A vigorous exothermic reaction was noted when the temperature reached 45°C., sufficient to bring the reaction mixture to reflux. Two dry ice traps caught all the vapors not returned by the water condenser. Distillation of the contents of the traps yielded approximately ten ml. of methylene fluorobromide, about a 40 per cent yield. The boiling point range was 17.5 to 19.5°C.

Methylene Fluoroiodide.--Attempts to prepare methylene fluoroiodide by decomposition of silver fluoroacetate with iodine in nitrobenzene solution yielded, after 45 minutes at 100°C. and 100 mm. pressure, a small amount of cold trap condensate. Fractional distillation gave about two ml. of a hazy liquid boiling 48-50°C. (n_D^{20} 1.442). Although the boiling point agreed reasonably, the refractive index was rather lower than that reported by Van Arkle and Janetzky (13).

Reaction of an excess of methylene iodide with aqueous silver fluoride was tried next. The two immiscible layers were violently stirred at a temperature of 60°C. for about three hours in a three necked flask fitted with a condenser. Stirring was discontinued and the temperature slowly raised without noticeable distillation to 95°C. A cloudy distillate was obtained (95-100°C.) which separated upon standing to yield much of the reactant methylene iodide. Although the pot contained what apparently was silver iodide, nothing resembling the desired product could be anywhere detected.

---

(13) A. E. Van Arkle and E. Janetzky, Rec. trav. chim., 56, 167 (1937).

Methylene fluoroiodide was successfully synthesized by S_N2 displacement of bromide from the fluorobromide by iodide ion. About 100 grams of freshly prepared methylene fluorobromide was added to approximately half a liter of methyl ethyl ketone. An excess of sodium iodide was introduced, the greater part of which remained undissolved. After 16 hours in the dark, the solid salts were removed by filtration, followed by distillation in the dark and under nitrogen. About 5 ml. of distillate was collected, containing 87 per cent of the desired product as indicated by infinity reaction titers.

Acetone.--Commercial acetone was purified by the method of Conant and Kirner (10) and stored in a brown bottle under nitrogen. Although acetone purified in this manner is not completely dry (14), the method is reproducible as indicated by constant rate constants for reactions run in different batches of solvent.

Potassium Iodide.--Reagent grade potassium iodide was dried in a vacuum oven at 160°C. overnight and used immediately thereafter.

Ethyl Bromide.--Merck reagent grade ethyl bromide was distilled and the fraction boiling at 38.6°C. (n_D^{20} 1.4243) was collected and stored in the usual manner.

Standard Methanolic Iodine.--An accurately weighed sample of C. P. iodine was dissolved in dry methanol, standardized against C. P. sodium thiosulfate and stored in a brown bottle. The titer increased less than one-half per cent within two months.

---

(14) A. R. Olson, L. D. Frashier and F. J. Spieth, J. Phys. Chem., 55, 860 (1951).

Potassium Iodate.--Baker's Analyzed, C. P. potassium iodate was weighed as a primary standard and dissolved in water to form a 0.01556 N solution as an oxidizing agent.

Chloromethyl Phenyl Thioether.--An attempt was made to prepare chloromethyl phenyl thioether by the method of Böhme (15, 16). This compound would have provided a way of measuring the rate of the second step of the thiophenolate, chloromethyl halide reactions. Analysis of the distilled fractions from two runs, collected at 98°C. and 12 mm., by hydrolysis and methanolysis followed by titration of the hydrochloric acid produced, indicated a maximum yield of eight per cent of the desired compound. The preparation reaction

$$C_6H_5SH + CH_2O + HCl_{(g)} \rightleftarrows C_6H_5SCH_2Cl + H_2O$$

is best run at -15°C. in presence of a dessicant. As in (16), calcium chloride was employed. In light of the poor yield, it is possible that dehydration, which must be successful prior to a rise in temperature above -5°C., was incomplete, and that better results would have been obtained with a more efficient desiccant.

---

(15) H. Böhme, Ber., 69B, 1610 (1936).

(16) H. Böhme, H. Fischer and R. Frank, Ann., 563, 54 (1949).

CHAPTER III

RESULTS

Toward thiophenolate in methanol, methylene halides containing no fluorine undergo consecutive displacement of both halogens.

$$C_6H_5S^- + CH_2XY \xrightarrow{k_1} C_6H_5SCH_2Y + X^-$$

$$C_6H_5S^- + C_6H_5SCH_2Y \xrightarrow{k_2} (C_6H_5S)_2CH_2 + Y^-$$

Under identical conditions, fluoromethyl bromide and iodide react to give fluoromethyl phenyl thioether which is resistant to further attack. The specific rate constants for the latter reactions were calculated from the integrated, second order rate equation

$$k = \frac{2.303}{t(a_o - b_o)} \log\left(\frac{b_o}{a_o}\right)\frac{a}{a - (a_o - b_o)} \qquad (1)$$

where $\underline{a}_o = [C_6H_5S^-]_o$, $\underline{b}_o = [FCH_2X]_o$, $\underline{a} = [C_6H_5S^-]_t$ and $\underline{t}$ = time in seconds.

For the other methylene halides the rate equation was derived under the assumption that displacement of the first halogen is followed by very rapid displacement of the second

$$k_1 = \frac{2.303}{t(a_o - 2b_o)} \log\left(\frac{2b_o}{a_o}\right)\frac{a}{a - (a_o - 2b_o)} \qquad (2)$$

where $\underline{b}_o = [CH_2XY]_o$ and $\underline{a}$, $\underline{x}$, and $\underline{t}$ have the same significance as before.

It may be shown, e.g., by the method of Frost and Schwemer (17), that reactions characterized by $K = k_2/k_1 > 10$ are satisfactorily fit by equation (2). For example, for a reaction where $K = 10$ and $2b_o = a_o$, if the rate constants are calculated by means of equation (2), from 20 per cent to 60 per cent of a, they climb over a range of about five per cent, an effect upon each point smaller than the average deviation caused by experimental error.

Of all the methylene halides studied, methylene chloroiodide should be most likely to deviate noticeably, as indicated by rising rate constants within a given run. At 0°C., points taken at 19.7 and 35.3 per cent reaction yielded somewhat lower rate constants than were obtained between 42 and 70 per cent reaction. Over the latter range of 28 per cent the rate constants calculated were, in effect, constant, showing no tendency to rise or fall. At 40°C. no such effect is noticeable. Whether the rise at 0°C. is due to a small k_2/k_1 ratio or experimental error is problematical; noting that a rise induced by the former effect is always toward the true value of k_1, this constant was calculated by averaging all points except the earliest.

The rate constants calculated for the other methylene halides were consistent, as judged by constancy during a given run, with the mechanism assigned. All these data may be found in Table 1. Within an individual run, points taken before 4 minutes and/or 15 per cent reaction and after 90 per cent reaction, and those whose deviations were more than four times the average were rejected. For each compound, the tabulated enthalpy and entropy of activation are the averages of the two values calculated for

---

(17) A. A. Frost and W. C. Schwemer, J. Am. Chem. Soc., 74, 1268 (1952).

each parameter, by means of the absolute rate equation (18), from the opposed extremes of the rate constants at the two temperatures. The tabulated uncertainty is half the difference between the two calculated values.

Although iodides are considerably more reactive than the corresponding bromides, (the ease of displacement of halogens from carbon usually increases with increasing atomic number), methylene bromoiodide undergoes both displacements. By assuming the reaction rate for bromomethyl bromide is to that for iodomethyl bromide as the reaction rate for bromomethyl iodide is to that for iodomethyl iodide, the contributions of both to the overall rate constant may be estimated.[1] At zero degrees from Table 1

$$\frac{.0798 \times 10^{-4}}{(.811 \times 10^{-4}) - y} = \frac{y}{1.19 \times 10^{-4}} \quad \text{(or)}$$

$$y = 0.669 \times 10^{-4} \text{ l./m.s.}$$

$$(0.811 \times 10^{-4}) - y = 0.142 \times 10^{-4} \text{ l./m.s.}$$

where y is the rate constant for displacement of bromine from methylene bromoiodide by sodium thiophenolate.

At 40°C., the respective values are

$$y = 62.5 \times 10^{-4} \text{ l./m.s., and}$$

$$(79.8 \times 10^{-4}) - y = 17.3 \times 10^{-4} \text{ l./m.s.}$$

---

[1] We are concerned only with the displacement, in the first step, of iodide when the methylene halide is labeled as bromomethyl iodide and only with displacement, in the first step, of bromide when labeled as iodomethyl bromide. The measured value of k_1 is of course the sum of the rates for both displacements.

(18) S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

Table 1. Kinetic Constants for Reactions of Methylene Halides with Sodium Thiophenolate in Methanol

Halide	$10^4 k_1$ (l./m.s.) 0.0°C.	40°C.	ΔHa Kcal.	ΔSa e.u.
ICH_2I [1]	1.19 ± .01	108 ± 2	18.6 ± 0.1	-8.5 ± 0.4
$BrCH_2I$	0.811 ± .018	79.8 ± 1.6	18.9 ± 0.2	-7.9 ± 0.6
$ClCH_2I$	1.83 ± .03	149 ± 3	18.1 ± 0.2	-9.2 ± 0.7
FCH_2I	47.9 ± .9	964 ± 20 [2]	15.9 ± 0.2	-10.8 ± 0.8
$BrCH_2Br$ [1]	0.0798 ± .0004	10.0 ± .2	20.0 ± 0.2	-8.7 ± 0.5
$ClCH_2Br$	0.228 ± .002	25.1 ± .3	19.4 ± 0.1	-8.6 ± 0.3
FCH_2Br	1.88 ± .03 [4]	152 ± 5	18.1 ± 0.2	-9.2 ± 0.8
$ClCH_2Cl$ [1]	0.0214 ± .0010 [3]	0.222 ± .007	21.1 ± 0.7	-12.5 ± 2.6

[1] Rate constants contain a statistical factor of one-half.

[2] At 30°C.

[3] At 20.35 °C.

[4] Value in reference (5) is in error.

By similarly assuming the reactivity of n-propyl bromide is to that of ethyl bromide as the reactivity of n-propyl iodide is to that of ethyl iodide, from Table 1 and reference (5).

$$y = 21.76 \times 10^{-4} \text{ l./m.s.}$$

where y is now the rate constant for displacement of iodine from ethyl iodide by sodium thiophenolate at zero degrees. It should be borne in mind that these estimates are not entirely reliable since they are based on assumptions of a type shown by other data in Table 1 to be not generally true.

The rate equation for competitive consecutive second order reactions may be integrated, assuming $k_2 = \frac{k_1}{2}$, to give an expression similar to equation (2) except for a constant. Under this assumption,

$$k_1(K = 1/2) = 2k_1(K = \infty) = \frac{2(2.303)}{t(a_o - 2b_o)} \log\left(\frac{2b_o}{a_o}\right)\frac{a}{a - (a_o - 2b_o)} \qquad (3)$$

Therefore, if within a given run the rate constants (k_1) calculated remain constant, either the second step proceeds much more rapidly than the first or K = 1/2. From knowledge of the displacement rates of, and the effects exercised as alpha substituents by halogens, the latter possibility may be immediately excluded for all methylene halides except methylene

chloroiodide.[1] If for methylene chloroiodide, K = 1/2, then it is apparent from Table 1 that K = 6 for methylene chlorobromide at 40°C. The rate constants computed for the latter by equation (2) drift upward slightly over the range 22 to 54 per cent reaction, their behavior when K = 6 is ascertained as follows.

The rate equations for competitive consecutive second order reactions in general are not amenable to closed form integration unless $2b_o = a_o$ and $\underline{K}$ is rational. At 40°C., $[C_6H_5S^-]_o \neq 2[CH_2ClBr]_o$. The following approximative technique, which is a generalization (with respect to the initial concentrations of the reactants) of the method discussed in reference (17), has therefore been employed.

In general form,

$$- da/dt = k_1ab + k_2ac \qquad (4)$$

$$- db/dt = k_1ab \qquad (5)$$

where $c = [C_6H_5SCH_2Y]_t = 2(b_o - b) - (a_o - a)$.

Substituting for $\underline{c}$ in equation (4) and dividing the result by equation (5) yields,

---

[1]For example, if K = 1/2 for the reaction of methylene chlorobromide at forty degrees, k_2 = 25.1 l./m.s. The value of k_2 for methylene chloroiodide would also have to have this value, making the second step of this reaction much slower than the first. Since equation (2) yields constant rate constants, this cannot be.

If K = 1/2 for bromomethyl iodide at forty degrees, then k_2 = 62.5 l./m.s. But we have just gathered that k_2 for methylene chlorobromide is equal to or greater than about 250 l./m.s. This would have the intermediate chloride considerably more reactive than the bromide which is not reasonable.

$$da/db = 1 + K\left(\frac{a - 2b}{b}\right) - K\left(\frac{a_o - 2b_o}{b}\right) \tag{6}$$

$$= (1 - 2K) + a\left(\frac{K}{b}\right) - \frac{K(a_o - 2b_o)}{b}$$

which is a linear differential equation of the first order.[1]

Integration between the respective limits of a_o to a, and b_o to b yields,

$$a = (a_o - 2b_o) + \frac{1 - 2K}{1 - K} b + \frac{b_o}{1 - K} \left(\frac{b}{b_o}\right)^K \tag{7}$$

Substituting equation (7) into equation (5) and letting $B = b/b_o$,

$$T = b_o k_1 \int_o^t dt = \int_B^1 \frac{dB}{B\left[\frac{1}{1 - K} B^K + \frac{1 - 2K}{1 - K} B + \frac{a_o - 2b_o}{b_o}\right]} \tag{8}$$

Any desired degree of approximation of the right hand integral may be obtained from Simpson's Method.[2]

$$\int_B^{B'} f(B)\, dB = \frac{B' - B}{6n} \left[Y_o + 4Y_1 + 2Y_2 + \cdots\cdots + Y_{2n}\right] \tag{9}$$

where 2n is the number of equal parts into which the interval of integration is divided and, $Y_i = f(B_i)$, $i = 0,1 \ldots 2n$.

---

[1] For a general method of solution, see any advanced calculus text, e.g., I. E. and E. S. Sokolnikoff, Higher Mathematics for Engineers and Physicists, 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 284.

[2] Ibid., p. 556.

For the reaction of methylene chlorobromide and thiophenolate at 40°C., a_o = 0.03931 M, b_o = 0.04416 M, K = 6 and $(a_o - 2b_o)/b_o$ = -1.110. Choosing B intervals of 0.08 and n = 4 for each of these intervals, T was calculated as a function of B and, from equation (7), as a function of $A = a/a_o$. From a plot of T against A (Fig. 1), a value of T for each point is obtained. Knowing the reaction times allows calculation of the rate constants k_1 from the left side of equation (8). Table 2 contains the experimental data as well as the rate constants calculated for both K values.

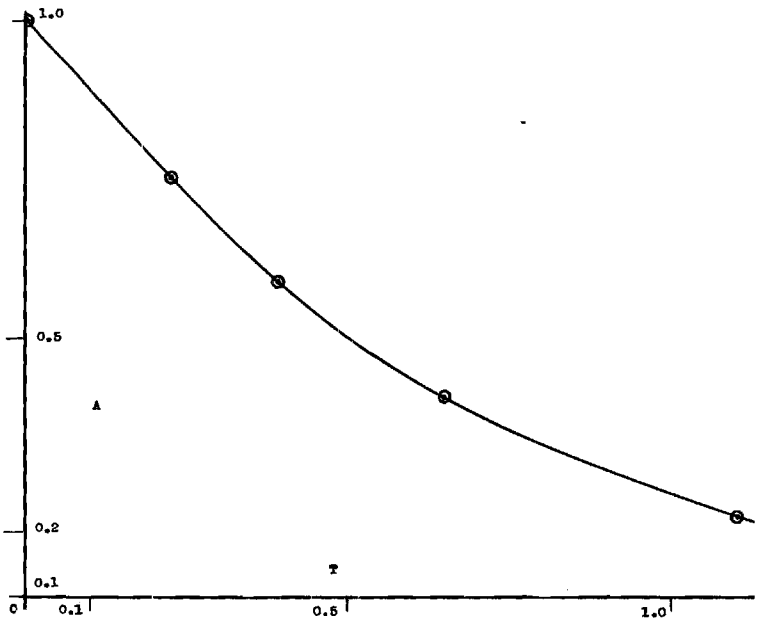


Fig. 1. Parameter A versus the Time Parameter T

Table 2. $CH_2ClBr + C_6H_5SNa$ in Absolute Methanol at 40°C.

CH_2ClBr 0.04416 M — Methanolic Iodine 0.0302 M

C_6H_5SNa 0.03931 M — 20 ml. samples

			$10^4 k_1$ (l./m.s.)	
Time in Seconds	ml. of I_2	A	K = ∞	K = 6
0	26.03	1.000	---	---
1175	20.38	.780	24.87	37.6
1495	19.18	.735	24.70	36.1
1845	17.86	.685	25.04	35.0
2320	16.21	.622	25.50	34.1
3235	13.79	.528	25.27	32.5
3975	12.09	.464	25.40	31.7

Average k (K = ∞) $(25.13 \pm 0.25) \times 10^{-4}$ l./m.s.

(K = 6) $(34.5 \pm 1.7) \times 10^{-4}$ l./m.s.

It is apparent that for $K = 6$, the rate constants calculated exhibit relatively strong downward deviations during the run; this provides satisfactory evidence that $K \neq 6$ for methylene chlorobromide and $K \neq 1/2$ for methylene chloroiodide at 40°C. A similar hypothesis at zero degrees could not be as conclusively tested since the rate constants obtained when K equal eight (for methylene chlorobromide) are not likely to be easily distinguishable in practice from those obtained when K is infinity.

However, if $K = 1/2$ at zero degrees, the temperature coefficient of reaction rate for the second step over the 40 degree range would be six times that for the first step, suggesting a much higher free energy of reaction for the intermediate than for the dihalide. This conclusion disagrees with the data for the other dihalides and the known effects of thiophenyl substitution upon rate.

The reactions of alkyl halides with sodium and potassium iodide in acetone are known to be, in some cases, appreciably reversible (3,10) and prone to complication by alkali halide precipitation. For the particular case of ethyl bromide, it was noted by Dostrovsky and Hughes at 64°C. employing both iodide salts (3) and Thomas at 20.3°C. using sodium iodide (8) that rate constants calculated from the integrated second order rate equation fell sharply as the reaction proceeded. This fall was attributed to reversibility.

Runs conducted with potassium iodide resulted in falling S_N2 rate constants at both zero and twenty degrees, confirming the former findings. The drop at the lower temperature was much less severe than at the higher. At twenty degrees rate constants were also calculated assuming reversibility by the following equation

$$k = \frac{2.303}{qt} \log \frac{(a_o + b_o - q)\,[2(1 - K)a + b_o + a_o(2K - 1) + q]}{(a_o + b_o + q)\,[2(1 - K)a + b_o + a_o(2K - 1) - q]} \quad (10)$$

where $\underline{a_o} = [I^-]_o$, $\underline{b_o} = [C_2H_5Br]_o$, $\underline{q} = [(b_o + a_o(2K - 1))^2 + 4Ka_o^2(1 - K)]^{\frac{1}{2}}$, $\underline{a} = [I^-]_t$ and $\underline{t}$ = time in seconds. $\underline{K} = k_2/k_1 = (a_\infty)(b_\infty)/(a_o - a_\infty)(b_o - a_\infty) =$ 0.358. The rate constants calculated by both mechanisms are contained in Table 19.

The assumption of reversibility, while raising the later rate constants slightly relative to the earlier, does not satisfactorily account for the drop. In event of precipitation of potassium bromide the reverse reaction would be suppressed and the rate constants calculated by equation (10) would rise. Incomplete ionization of potassium iodide in acetone (sodium (19) and lithium iodides are weak electrolytes in this solvent), would result in rising S_N2 rate constants. It is apparent therefore that none of the phenomena that are known to occur during the reaction provide sufficient explanation of the observed deviations.

Rate constants were obtained at both temperatures by extrapolation to zero time of the calculated rate constant versus time plots. At twenty degrees, the constants for both mechanisms extrapolated to the same value and agreed with Thomas', (k = 0.00123 at 20.3°C.), obtained by a different method of extrapolation. Since the completion of this study, Fowden, et. al. (20) have published kinetic data on several of the Finklestein reactions. The rate constants for ethyl bromide reaction with sodium and potassium iodide at 20°C. (k = 0.00117 and 0.00120, respectively), reportedly

---

(19) C. A. Kraus and W. C. Bray, J. Am. Chem. Soc., 35, 1315 (1913).

(20) L. Fowden, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 3187 (1955).

uncomplicated by either reversibility or precipitation for the first fifty per cent of reaction, agree well with the values obtained by extrapolation. It is of interest to note that the rate constant for reaction with lithium iodide is 15 per cent smaller (20).

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The following generalizations are possible concerning the effects of structure on reactivity of the methylene halides toward thiophenolate.

The relative order of deactivation for alpha substituent halogens noted in both the iodide and methoxide reactions is maintained, with greater quantitative similarity to the reactions of iodide ion.[1] Deactivation due to substituent bromine is greater than that due to iodine. Flourine deactivation is greater than methyl in bromide (21), but apparently not in iodide, displacement. For all cases within the observed temperature range, the more reactive a methylene halide the smaller is its enthalpy of activation. Whether, in light of their appreciable uncertainties, the differences in the entropies of activation contribute to the difference in reactivity is not estimable.

Considering the nature of the substituents and position of substitution, replacement of hydrogen by halogen in the methyl halides should result in appreciable steric and inductive effects upon the S_N2 reactivity. It is apparent from examination of the reactivity data for the three nucleophile systems that such effects are indeed important; however it is believed that they cannot alone account for the overall deactivations noted.

---

[1] Data on the iodide and methoxide reactions are to be found in Reprints of Tables II and IV from Journal Reference (1); in the Appendix, Tables 21 and 22.

(21) J. Hine and W. H. Brader, Jr., J. Am. Chem. Soc., 75, 3964 (1953).

Toward the strong nucleophiles, iodide and thiophenolate ions, the large deactivation effect of alpha fluorine appears to be primarily electronic (from considerations of the comparable size of fluorine and hydrogen (22), and the effect of similar substitution in the beta position of ethyl bromide (21)). The heavier halogens should exercise less of an inductive effect, which apparently is deactivating, but considerably more of a steric deactivation effect than fluorine. This is possible to demonstrate roughly. If the assumption that substituent bromine and methyl exercise similar steric effects because of their similar van der Waal radii (22) is legitimate,[1] from the estimation by de la Mare, et. al. (23) that alpha methyl deactivation in the bromide exchange reactions is about 14 fold steric and 5 fold electronic we may estimate that the steric effect due to bromine in the iodide displacement of bromide is on the order of 30 fold compared to a 350 fold electronic factor. To arrive at the later estimation, the assumption has been made that the difference in deactivation of alpha sutstituent methyl toward iodide ion compared to that toward bromide

---

[1]Confidence in the correlation of steric effects with such measures of size as the van der Waal radii must be limited. The effective blocking volume of a group depends to some extent upon the species it blocks. This is quite plainly indicated by Streitwieser (24) who discusses S_N2 steric effects partly in terms of antibonding p orbital overlap between the substituent and respectively the nucleophile and the departing group. It is of interest to note that covalently bound heavier halogens are capable of bonding overlap with ions to form complexes, viz. I_3^-, a property which may render them less effective sterically than the van der Waal radii indicate.

(22) L. Pauling, The Nature of the Chemical Bond, 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189.

(23) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, J. Chem. Soc., 3200 (1955).

(24) A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).

ion is entirely steric; toward iodide ion methyl deactivates overall by a 140 fold factor (23).

To account for the smaller deactivation effect of bromine compared to chlorine than for chlorine compared to fluorine, it appears that the decreases in electronic deactivation passing from fluorine to chlorine to bromine must be smaller than the concurrent increases in steric hindrance, with the greater difference for the first change. On the other hand, the decrease in electronic deactivation must be greater than the steric increase to explain the overall decrease in deactivation passing from bromine to iodine in these terms.

Induction as the sole electronic effect cannot reconcile the strong deactivation accompanying replacement of fluorine by chlorine (compared to that for bromine substitution for chlorine), and the comparative bromine and iodine effects. While the van der Waal radii difference between fluorine and chlorine is three times that between the latter and bromine, the electronegativity difference is five times as great. If the sensitivity to electronegativity differences is minimized, the bromine-iodine order cannot be explained.

Examination of the structural properties of the methylene halides indicates that at least one other electronic factor than inductive withdrawal by the substituent is likely to affect the S_N2 reactivity.

Carbon-halogen bond lengths are shortened by introduction of a second halogen into the methyl halides. Pauling (25), from considerations of electron diffraction data, and other investigators from microwave spectral

---

(25) L. Pauling, op. cit., p. 235.

studies (26, 27) on the chlorine and fluorine halides of methene, attribute this shortening to π bond structures, e.g., ($^{+}Y = CH_2 X^{-}$), which are impossible in the methyl halides. Although it is difficult to estimate the relative π bonding abilities of chlorine and fluorine from these data quantitatively because of the concurrent inductive effects, it appears fluorine is somewhat superior. Pauling roughly estimated it to be twice as good. Presumably bromine and iodine exhibit further decreases in this faculty, although there are no conclusive data on their methylene dihalides presently available.[1]

It is of interest to note that such π bond formation is held responsible for the strong activation effect of alpha substituent alkoxy groups, Y equal RO above, (28).

Consider the reactivities of the methylene halides where the displaced halogen remains the same while the substituent is varied. Of the two π bond structures it is possible to write, the contribution of one, where Y (above) is the departing halogen, varies as a function of the inductive ability of the substituent (X) and is included under that effect.

---

[1] See the compilation of halomethane bond distances in G. W. Wheland, Resonance in Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1955, Appendix. While much of the data, including most of that on the bromides and iodides, have been obtained from electron diffraction studies and therefore have relatively large uncertainties, it appears that shortening is of importance only for the carbon-fluorine and, to a much smaller degree, for carbon-chlorine bonds. In the tetrahalomethanes some bond lengthening is noted which likely is the result of steric repulsions between the halogens.

(26) N. Muller, J. Am. Chem. Soc., 75, 860 (1953).

(27) D. R. Lide, Jr., ibid., 74, 3548 (1952).

(28) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Presst, J. Chem. Soc., 3641 (1955).

The contribution of the other, ($^{+}Y = CH_2 X^{-}$) with X departing, which is a reactive structure, varies with the π bonding ability of the substituent.[1]

Recalling that the substituent is equally or more electronegative than the departing halogen in all cases (except for the minor reaction of methylene bromoiodide) and that the π bonding ability of the halogens decreases with decreasing electronegativity, the overall effect of π bonding should be activating. Therefore, it seems reasonable that the difference in the deactivations caused by the substituent halogens should not be as great as indicated by induction in terms of electronegativity differences. The greatest correction would be for fluorine, bringing its total electronic effect nearer chlorine's. Iodine should be subject to little change (little π bonding, small contributions of ionized structures to molecules in which it is the substituent).

Coupled with the previously noted differences in size, these corrections may account for the larger overall deactivation noted for the fluorine to chlorine, rather than chlorine to bromine change.

De la Mare and Hughes (29) attribute alpha halogen deactivation in S_N2 reactions to an interaction of such π bond effects with induction and to the exclusion of steric effects. Ignoring the latter seems a bit severe, especially in light of their earlier estimates (23).

---

[1] The contributions of the first and second structures respectively depend as well upon the π bonding and inductive abilities of the departing halogen. For the comparisons drawn, however, these effects should remain constant since only the substituent is varied.

(29) P. B. D. de la Mare and E. D. Hughes, ibid., 845 (1956).

That substituent iodine deactivates less than bromine appears to be due to the fact that iodine and carbon are equally electronegative, precluding strong inductive destabilization of the transition state.[1] Recalling the rough estimation of the steric and electronic effects of substituent bromine mentioned previously, if iodine has six times the steric effect of bromine it would still exercise about a twenty-five fold electronic deactivation effect.

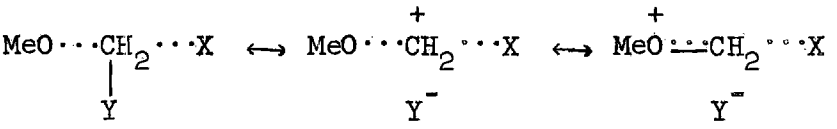
The significant difference noted in the methoxide reactions, other than the generally lower reactivities which were to be expected with a weak nucleophile, are the smaller deactivation effects exercised by the halogens. The difference is especially noticible for fluorine substitution. Toward iodide its deactivation effect is 400 fold, toward methoxide less than three fold. The other halogens are about ten times more efficient at deactivation in the reactions with strong nucleophiles than in the methoxide reactions. One might expect, recalling the effect of alpha alkoxy substituents upon S_N2 reactivity, that methoxide would, to some degree, stabilize the positive charge in the transition state through π bond formation.

---

[1] While not entirely satisfactory, electronegativity differences between carbon and the halogens are probably better measures of induction than the dipole moments of the bonds between these atoms. The large moment of the carbon-iodine bond is due, according to Pauling (30), not to electron withdrawal by iodine but to an unsymmetrical distribution of the electrons of the normal covalent bond and the unshared electrons of the iodine atom. The moments of the bonds between carbon and fluorine and chlorine are too small, according to Gordy, et. al.(31), because, in the ionic forms ($R_3{}^+ C X^-$), the electron density in the carbon orbitals directed toward the R groups is greater than that directed toward the halogen, giving a dipole with positive end toward the halogen, opposing the primary moment.

(30) L. Pauling, op. cit., p. 69.

(31) W. Gordy, W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. VII.



This would account at least in part for the differences in effects noted for the less electronegative halogens. Fluorine would not only participate in carbon-fluorine π bond structures but also would allow, by virtue of its strong induction, a much stronger contribution of the oxonium structure for the partially formed ether linkage. The resulting positive charge distribution might well cancel most of the inductive deactivation effect.

Since sulfur is able to form an equivalent of the oxonium ion, thiophenolate might be expected to show a similar effect to methoxide. That it does not to any appreciable extent, judging from the effects of fluorine compared to methyl substitution on bromide displacement by thiophenolate and iodide ions, is likely due to resonance stabilization of the reactant ion by semiquinoid structures. This is to some extent borne out by the data of Kirner and Richter (32), and Conant, et. al. (33), reproduced in Table 3. It is possible that the beta thiomethyl group may activate the displacement of chloride by a ring sulfonium ion structure, while the small negative charge of sulfur in the thiophenyl group is held by resonance on the benzene ring precluding similar behavior.

The average enthalpies of activation are considerably greater for the reactions toward methoxide than toward iodide and thiophenolate, as are the activation entropies. Similar to the thiophenolate data, the enthalpy

---

(32) W. R. Kirner and G. H. Richter, J. Am. Chem. Soc., 51, 3409 (1929).

(33) J. B. Conant, W. R. Kirner, and R. E. Hussey, ibid., 47, 476 (1925).

Table 3. Relative Rates of Chloride Displacement by Iodide Ion in Acetone at 50°C.

Compound		Compound	
$\underline{n}C_4H_9Cl$	1.0	$\underline{n}C_3H_7Cl$	1.1
$CH_3SCH_2CH_2Cl$	1.5	$C_6H_5CH_2CH_2Cl$	1.1
$C_6H_5SCH_2CH_2Cl$	0.56	$C_6H_5CH_2CH_2CH_2Cl$	1.7
C_2H_5Cl	2.5		

orders are for both iodide and methoxide, with very few exceptions, the inverse of the respective rate constant orders. In general, of similar reactions, those that are faster under a given set of conditions have smaller enthalpies of activation. This should both account for the order toward a given nucleophilic agent and the differences noted between the nucleophiles.

The entropy of activation is quite sensitive to steric effects and, although generalizations from the data of a single nucleophile are impossible here, it is of interest to note the overall differences between the smaller methoxide and larger iodide and thiophenolate ions. While it might not have been predicted, it does not seem unreasonable that the methoxide reactions are characterized by larger activation entropies. The oxonium ion structures, it is true, deprive the transition state of one degree of freedom, rotation around the forming carbon-oxygen bond. However, the greater bulk of the other nucleophiles may also, to some extent, restrict the motions within their respective transition states and therefore decrease the activation entropies.

While the thiophenolate displacement of bromide is more strongly deactivated by fluorine than by methyl substitution, the reverse is true for

iodide displacement. This may be due to differences in π bond contributions and/or to greater compression by the neighboring methyl group upon iodine than upon bromine, requiring a greater bond breaking to making ratio in the transition state, and therefore also requiring a greater energy of activation for iodide displacement. A similar difference is noted between substituent fluorine and bromine in the bromide and iodide displacements. Bromine is about three times more effective at deactivation than fluorine in the iodide than in the bromide displacements.

CHAPTER V

RECOMMENDATIONS

From the viewpoint of the presented interpretation, perhaps the most valuable reactivity study at this time would involve a small, strong nucleophile, allowing a more conclusive separation of the steric and inductive effects accompanying alpha halogen substitutions. Cyanide ion, a slightly stronger nucleophile than iodide, is suggested (34).

Studies of the reactions of the methylene halides with triethylamine and quinuclidine have been proposed (8) and would be of merit in consideration of steric factors.

Specifically to test the supposition of oxonium bond stabilization of the transition state by methoxide, several runs with an alkyl mercaptide should be conducted.

Emphasis should not only be placed on reactivity studies. Such information as precise bond length data for the bromine and iodine containing methylene halides, and the effects of solvation on the properties of the species involved in the reactions would be of much value. Very little is known of the apparently important solvation effects, especially in non-aqueous media, and, unfortunately, it appears difficult at this time to learn much more.

---

(34) M. F. Hawthorne, G. S. Hammond and B. M. Graybill, ibid., 77, 486 (1955).

APPENDIX

TABLES

Table 4. CH_2I_2 + C_6H_5SNa in Absolute Methanol at 0°C.

CH_2I_2 0.01738 M — I_2 0.0304 M

C_6H_5SNa 0.04888 M — 15 ml. aliquots

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	24.12	---
25530	20.01	1.213
64740	16.22	1.209
70140	15.85	1.205
87860	14.82	1.188
93120	14.59	1.174
117510	13.42	1.181
154620	12.11	1.183
172650	11.56	1.196

Rate constants contain statistical factor of two.

Average k = (1.193 ± 0.012) x 10^{-4} l./m.s.

Table 5. CH_2I_2 + C_6H_5SNa in Absolute Methanol at 40°C.

CH_2I_2 0.01440 M — I_2 0.0304 M

C_6H_5SNa 0.02412 M — 20 ml. samples

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	15.87	---
630	11.41	104.4
975	9.68	108.3
1140	9.06	108.0
1335	8.46	106.5
1575	7.67	108.7
1775	7.07	110.9
2325	6.01	108.6

Rate constants contain statistical factor of two.

Average k = (107.9 ± 1.4) x 10^{-4} l./m.s.

Table 6. $CH_2BrI + C_6H_5SNa$ in Absolute Methanol at 0°C.

CH_2BrI 0.03048 M — I_2 0.0304 M

C_6H_5SNa 0.04827 M — 15 ml. samples

Time in Minutes	ml of I_2	$10^4 k$ (l./m.m.)
0	23.82	---
625.5	19.86	51.09
1265.0	17.02	49.66
1408.5	16.51	49.26
1929.5	14.78	48.91
2891.0	12.37	48.00
3268.0	11.64	47.49
4032.0	10.14	48.35
4710.5	9.39	46.41

Average $k = (48.65 \pm 0.96) \times 10^{-4}$ l./m.m.

$= (0.811 \pm 0.16) \times 10^{-4}$ l./m.m.

Table 7. $CH_2BrI + C_6H_5SNa$ in Absolute Methanol at 40°C.

CH_2BrI 0.02539 M — I_2 0.0304 M

C_6H_5SNa 0.05235 M — 15 ml. samples

Time in Seconds	ml of I_2	$10^4 k$ (l./m.s.)
0	25.83	---
555	21.27	80.08
930	18.76	82.65
1320	16.90	81.35
1890	14.71	81.18
2280	13.49	81.45
3060	11.72	80.10
3675	10.64	79.27
4380	9.62	78.80
5550	8.38	77.26
7215	7.09	76.08

Average $k = (79.82 \pm 1.58) \times 10^{-4}$ l./m.s.

Table 8. CH_2ClI + C_6H_5SNa in Absolute Methanol at 0°C.

CH_2ClI	0.01643 M	I_2	0.04955 M
C_6H_5SNa	0.04489 M	15 ml. samples	

Time in Minutes	ml. of I_2	10^4k (l./m.m.)
0	13.59	---
1074.5	10.08	105.3
1320.0	9.42	111.1
1553.5	9.02	109.6
2747.0	7.39	110.9
2937.5	7.21	110.6
3212.0	6.95	111.3

Average k = (109.8 ± 1.6) x 10^{-4} l./m.m.

= (1.83 ± 0.03) x 10^{-4} l/m.s.

Table 9. CH_2ClI + C_6H_5SNa in Absolute Methanol at 40°C.

CH_2ClI	0.02254 M	I_2	0.04955 M
C_6H_5SNa	0.05143 M	15 ml. samples	

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	15.57	---
740	10.55	147.4
1055	9.34	147.1
1340	8.29	154.9
1605	7.67	153.6
2035	6.92	149.7
2620	6.10	148.1
3520	5.25	144.8

Average k = (149.4 ± 2.9) x 10^{-4} l./m.s.

Table 10. $CH_2FI + C_6H_5SNa$ in Absolute Methanol at 0°C.

CH_2FI 0.02407 M — I_2 0.05540 M

C_6H_5SNa 0.03565 M — 10 ml. samples

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	6.42	---
1775	5.38	48.19
2395	5.11	47.99
3605	4.67	48.07
6020	3.98	50.47
12245	3.22	46.16
14500	3.01	47.22
15545	2.94	47.13

Average k = (47.89 ± 0.90) x 10^{-4} l./m.s.

Table 11. $CH_2FI + C_6H_5SNa$ in Absolute Methanol at 30°C.

CH_2FI 0.03080 M — I_2 0.05540 M

C_6H_5SNa 0.04230 M — 10 ml. samples

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	7.64	---
240	4.72	942.5
430	3.81	944.9
1265	2.50	994.4
1710	2.32	974.2

Average k = (964.0 ± 19.3) x 10^{-4} l./m.s.

Table 12. CH_2Br_2 + C_6H_5SNa in Absolute Methanol at 0°C.

CH_2Br_2 0.03519 M — I_2 0.04915 M
C_6H_5SNa 0.05977 M — 15 ml. samples

Time in Minutes	ml. of I_2	10^4k (l./m.m.)
0	18.25	---
2212.5	15.86	4.758
4028.0	14.29	4.774
4682.0	13.74	4.849
5971.5	12.91	4.764
6887.0	12.32	4.786

Rate constants contain statistical factor of two.

Average k = (4.786 ± 0.025) x 10^{-4} l./m.m.

= (0.0798 ± 0.0004) x 10^{-4} l./m.s.

Table 13. CH_2Br_2 + C_6H_5SNa in Absolute Methanol at 40°C.

CH_2Br_2 0.07245 M — I_2 0.03020 M
C_6H_5SNa 0.03834 M — 20 ml. samples

Time in Seconds	ml. of I_2	10^4k (l./m.s.)
0	25.39	---
910	19.51	10.32
1195	18.38	9.71
1315	17.79	9.75
1555	16.70	9.78
1945	14.91	10.05
2435	12.86	10.41
3080	11.20	10.03

Rate constants contain statistical factor of two.

Average k = (10.01 ± 0.22) x 10^{-4} l./m.s.

Table 14. CH_2ClBr + C_6H_5SNa in Absolute Methanol at 0°C.

CH_2ClBr 0.1676 M
C_6H_5SNa 0.06830 M
I_2 0.03026 M
10 ml. samples

Time in Minutes	ml. of I_2	10^4k (l./m.m.)
0	22.57	---
1058.5	14.28	13.45
1115.3	13.84	13.67
1282.8	12.95	13.57
1558.5	11.46	13.75
1573.5	11.39	13.80
1859.8	10.08	13.83
2823.0	6.86	13.78

Average k = (13.69 ± 0.10) x 10^{-4} l./m.m.

= (0.228 ± 0.002) x 10^{-4} l./m.s.

Table 15. CH_2FBr + C_6H_5SNa in Absolute Methanol at 0°C.

C_6H_5SNa 0.02217 M
I_2 0.03026 M
Volume 40 ml.

Molarity CH_2FBr	Time in Minutes	ml. of I_2	10^4k (l./m.m.)
.02320	824	23.95	115.6
.03299	805	22.32	110.6
.06665	754	17.22	114.6
.04706	796	19.98	111.3
.06287	769	17.80	111.7
.10145	735	11.38	111.2

Average k = (112.5 ± 1.7) x 10^{-4} l./m.m.

= (1.88 ± 0.03) x 10^{-4} l./m.s.

Value in reference (5) is in error.

Table 16. $CH_2FBr + C_6H_5SNa$ in Absolute Methanol at 40°C.

C_6H_5SNa, run a 0.01976 M
run b 0.01231 M

I_2 0.03026 M
Volume 40 ml.

	Molarity CH_2BrF	Time in Seconds	ml. of I_2	$10^4 k$ (l./m.s.)
a	0.00660	1375	23.18	158.7
a	.00506	2540	22.74	149.7
a	.00939	2890	19.85	142.1
a	.01067	4185	17.27	150.1
a	.01558	1615	19.12	154.8
a	.01797	2025	16.79	157.3
a	.00985	1530	21.52	158.3
b	.00440	930	15.36	159.0
b	.00606	6290	11.50	142.1
b	.00365	6820	13.02	153.6
b	.00825	7195	9.47	148.6
b	.00522	5870	12.18	145.1

Average k = (151.6 ± 4.9) x 10^{-4} l./m.s.

Table 17. $CH_2Cl_2 + C_6H_5SNa$ in Absolute Methanol at 20.35°C.

CH_2Cl_2 0.04708 M
C_6H_5SNa 0.03581 M

I_2 0.0304 M
15 ml. samples

Time in Minutes	ml. of I_2	$10^4 k$ (l./m.m.)
0	17.67	---
6370	15.02	1.397
8962	14.16	1.367
11227	13.80	1.224
16160	12.32	1.294
17863	11.98	1.238
20180	11.49	1.222
24031	10.53	1.252

Rate constants contain statistical factor of two.

Average k = (1.285 ± 0.060) x 10^{-4} l./m.m.

= (0.0214 ± 0.0010) x 10^{-4} l./m.s.

Table 18. CH_2Cl_2 + C_6H_5SNa in Absolute Methanol at 40°C.

CH_2Cl_2 0.05947 M
C_6H_5SNa 0.06521 M
I_2 0.0554 M
10 ml. samples

Time in Minutes	ml. of I_2	10^4k (l./m.m.)
0	11.77	---
565.5	9.86	13.80
1179.0	8.31	13.60
1318.0	8.04	13.43
1574.0	7.49	13.08
1969.0	7.01	12.65
2003.0	6.95	12.67

Rate constants contain statistical factor of two.

Average k = (13.21 ± 0.41) x 10^{-4} l./m.m.

= (0.220 ± 0.007) x 10^{-4} l./m.s.

Table 19. C_2H_5Br + KI in Acetone at 20°C.

C_2H_5Br 0.04738 N
KI 0.02274 N
Aqueous KIO_3 0.01556 N
25 ml. samples

Time in Seconds	ml. of KIO_3	10^4k (l./m.s.) S_N2	10^4k (l./m.s.) equn.(10)
0	18.28	---	---
4140	14.91	10.85	10.84
5820	13.92	10.49	10.58
7200	13.30	10.00	10.08
10200	12.79	8.00	8.07
22200	9.17	7.61	7.90
33300	8.02	6.21	6.58
42600	6.64	6.17	6.84
45000	6.14	6.37	7.22
∞	3.41	---	---
Average 10^4k (l./m.s.)		8.21 ± 1.68	8.51 ± 1.49
Extrapolation to zero time (see p. 21)		11.7	11.8

Average extrapolated k = (12 ± 2) x 10^{-4} l./m.s.

Deviation taken equal to the average deviation.

Table 20. C_2H_5Br + KI in Acetone at 0°C.

C_2H_5Br 0.03040 N — Aqueous KIO_3 0.01556 N

KI 0.01211 N — 25 ml. samples

Time in Minutes	ml. of KIO_3	k x 10^4 (l./m.m.)
0	9.70	---
293	9.01	87.96
465	8.72	78.54
1260	7.54	69.84
2470	5.89	73.20
3700	5.07	64.98

Average k = (74.90 ± 6.22) x 10^{-4} l./m.m.

Extrapolation to zero time (see p. 21)

k = (84 ± 12) x 10^{-4} l./m.m.

= (14 ± 2) x 10^{-5} l./m.s.

Deviation taken equal to twice the average deviation.

Reprints of Tables II and IV from: J. Hine, C. H. Thomas and S. J. Ehrenson, J. Am. Chem. Soc., 77, 3886 (1955).

Table 21

KINETIC CONSTANTS FOR REACTIONS WITH IODIDE ION IN ACETONE

Halide	10^5k(l. mole^{-1} sec.$^{-1}$) 20.3°	36°	50°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
CH_3Br[a]	22,900[b]	276[c]		15.9 ± 1.0	−7.2 ± 3
CH_3CH_2Br	120 ± 20[d]	14 ± 2[d,e]	1700 ± 200[d]	16.4 ± 2.0	−16.0 ± 6
FCH_2Br	64 ± 10		1350 ± 18	18.8 ± 1.2	−9.1 ± 4
$ClCH_2Br$	7.32 ± 0.19	47.3 ± 0.5	218 ± 5	20.9 ± 0.5	−6.2 ± 2
$BrCH_2Br$[f]	2.03 ± 0.08	16.0 ± 0.4	69 ± 1	21.7 ± 1.2	−6.0 ± 4
ICH_2Br	5 ± 0.6[d]		100 ± 20[d]	18.4 ± 2.5	−15.5 ± 7
$ClCH_2Cl$[f]		0.842 ± 0.02[g]	0.211 ± 0.003	29.0 ± 1.0	+5.0 ± 3
ICH_2Cl			0.155 ± 0.005		

[a] From data of ref. 15c. [b] At 20.0°. [c] At −19.6°. [d] Estimated by extrapolation to zero time. [e] At 0.0°. [f] The observed rate constants have been divided by two to get the rate constants per bromine (or chlorine) shown. [g] At 60.0°.

Table 22

KINETIC CONSTANTS FOR REACTIONS WITH SODIUM METHOXIDE IN METHANOL

Halide	10^5k (l. mole^{-1} sec.$^{-1}$) 20.3°	50°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
CH_3I	14.9 ± 0.2	433 ± 9	20.8 ± 0.4	−5.2 ± 2
$ClCH_2I$	0.0863 ± .004	4.41 ± 0.16	24.4 ± 0.7	−3.1 ± 2
$BrCH_2I$	.031 ± .003[d]	1.02 ± .03	21.6 ± 1.0	−14.7 ± 4
ICH_2I[a]	.010 ± .002[d]	0.536 ± .007	24.7 ± 2.0	−6.4 ± 7
CH_3Br	17.1 ± .6	472 ± 24	20.5 ± 0.7	−5.9 ± 2
CH_3CH_2Br	1.33 ± .02	47.2 ± 1.6	22.0 ± 0.6	−5.9 ± 2
FCH_2Br	7.37 ± .14	225 ± 11	21.1 ± 0.7	−5.6 ± 2
$ClCH_2Br$[b]	0.0418 ± .001	2.36 ± 0.03	25.0 ± 0.4	−2.5 ± 2
$BrCH_2Br$[a,c]	0.00616 ± .0002	0.370 ± .02	25.4 ± 0.7	−4.9 ± 2
$ClCH_2Cl$[a]		0.0284 ± .001		

[a] The observed rate constants have been divided by two to get the rate constants per iodine (or per bromine or chlorine) shown. [b] At 36°, 10^5k = 0.378 ± 0.002. [c] At 36°, 10^5k = 0.0613 ± 0.002. [d] Estimated by extrapolation to zero time.

BIBLIOGRAPHY

General References

Ingold, C. K., Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

Sokolnikoff, I. S. and E. S., Higher Mathematics for Engineers and Physicists, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 284, 556.

Wheland, G. W., Resonance in Organic Chemistry, John Wiley and Sons, Inc., New York, N. Y., 1955, Appendix.

Literature Cited

(1) Hine, J., C. H. Thomas and S. J. Ehrenson, Journal of the American Chemical Society, 77, 3886 (1955).

(2) Petrenko-Kritschenko, P., V. Opotsky, M. Diakowa, and A. Losowog, Berichte der deutschen chemischen Gesellschaft, 62B, 581 (1929).

(3) Dostrovsky, I., and E. D. Hughes, Journal of the Chemical Society, 161 (1946).

(4) Brader, W. H., Jr., The Effect of Halogen Atoms on the S_N2 Reactivity of Other Halogen Atoms in the Same Molecule, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1954.

(5) Hine, J., S. J. Ehrenson, and W. H. Brader, Jr., Journal of the American Chemical Society, 78, 2282 (1956).

(6) Xan, J., E. A. Wilson, L. D. Roberts, and N. H. Horton, ibid., 63, 1139 (1941).

(7) Klason, P., and T. Carlson, Berichte der deutschen chemischen Gesellschaft, 39, 738 (1906).

(8) Thomas, C. H., The Effect of Halogen Atoms upon the S_N2 Reactivity of Other Halogen Atoms Attached to the Same Carbon Atom, Part I, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1953.

(9) Andrews, L. W., Journal of the American Chemical Society, 25, 756 (1903).

(10) Conant, J. B., and W. R. Kirner, ibid., 46, 232 (1924).

(11) Fieser, L. F., Experiments in Organic Chemistry, Part II, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 359.

(12) Haszeldine, R. N., Journal of the Chemical Society, 4259 (1952).

(13) Van Arkle, A. E., and E. Janetzky, Recueil des travaux chemiques des Pays-Bas, 56, 167 (1937)

(14) Olson, A. R., L. D. Frashier and F. J. Spieth, Journal of Physical Chemistry, 55, 860 (1951).

(15) Böhme, H., Berichte der deutschen chemischen Gesellschaft, 69B, 1610 (1936).

(16) Böhme, H., H. Fischer and R. Frank, Justus Liebigs Annalen der Chemie, 563, 54 (1949).

(17) Frost, A. A., and W. C. Schwemer, Journal of the American Chemical Society, 74, 1268 (1952).

(18) Glasstone, S., K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(19) Kraus, C. A., and W. C. Bray, Journal of the American Chemical Society, 35, 1315 (1913).

(20) Fowden, L., E. D. Hughes and C. K. Ingold, Journal of the Chemical Society, 3187 (1955).

(21) Hine, J., and W. H. Brader, Jr., Journal of the American Chemical Society, 75, 3964 (1953).

(22) Pauling, L., The Nature of the Chemical Bond, 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189.

(23) de la Mare, P. B. D., L. Fowden, E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, Journal of the Chemical Society, 3200 (1955).

(24) Streitwieser, A., Chemical Reviews, 56, 571 (1956).

(25) Pauling, L., op. cit., p. 235.

(26) Muller, N., Journal of the American Chemical Society, 75, 860 (1953).

(27) Lide, D. R., Jr., ibid., 74, 3548 (1952).

(28) Ballinger, P., P. B. D. de la Mare, G. Kohnstam, and B. M. Presst, Journal of the Chemical Society, 3641 (1955).

(29) de la Mare, P. B. D., and E. D. Hughes, ibid., 845 (1956).

(30) Pauling, L., op. cit., p. 69.

(31) Gordy, W., W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. VII.

(32) Kirner, W. R., and G. H. Richter, Journal of the American Chemical Society, 51, 3409 (1929).

(33) Conant, J. B., W. R. Kirner, and R. E. Hussey, ibid., 47, 476 (1925).

(34) Hawthorne, M. F., G. S. Hammond, and B. M. Graybill, ibid., 77, 486 (1955).

PART II

AN EMPIRICAL METHOD FOR PREDICTION OF THE BOILING POINTS OF THE HALOMETHANES

CHAPTER I

INTRODUCTION

Particular interest has been focused in this laboratory upon the halomethanes, many of which serve as substrates in nucleophilic displacement and haloform reactions. Since one of the most important criteria of identity for these compounds, the vast majority of which are liquids, are their normal boiling points, we have had occasion to check our values against those reported in the literature. In several cases we were surprised to find compounds credited with widely varying and occasionally quite unrealistic values for this property.

For example, two reports of the boiling point of dichlorodibromomethane were available; the first listed 150°C. (1), the second, 135°C. (2). The boiling point of fluorodiiodomethane was reported as 100.3°C. (3), 50°C. at 50 mm., which may be extrapolated to a normal boiling value of 122°C. (4), and 78°C. at 65 mm. (equivalent to about 147°C. at 760 mm.) (5). For several other compounds, different reports showed ten degree differences.

Examination of the pertinent data for a number of the halomethanes indicated that not only is the boiling point raised by substitution of a

---

(1) M. Arnhold, Ann., 240, 208 (1887).

(2) A. Besson, Compt. rend., 114, 222 (1892).

(3) O. Ruff, O. Bretschneider, W. Luchsinger, and G. Miltschitzky, Ber., 69, 299 (1936).

(4) R. N. Haszeldine, J. Chem. Soc., 4259 (1952).

(5) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.

heavier for a lighter halogen, but that the effect of a given change is nearly constant. Errors in several of the published reports could be spotted quite easily. For example, 147°C. appeared to be the most reliable of the three reports cited for fluorodiiodomethane.

In addition, substitution of a particular halogen for hydrogen was recognized to result in the same effect upon the boiling point only for compounds substituted to the same extent.

Taking both of these apparent regularities into consideration, correlation of the boiling points of the halomethanes as a linear function of the structure and kind of halogen(s) present was attempted. A summary of the techniques employed and the results obtained has recently been published (6). More complete details follow.

Historically, numerous attempts have been made without much success to relate boiling points theoretically to other physical properties of covalently bound molecules (7, 8, 9). The difficulty apparently lies in the lack of a good model for the liquid state (9).

Somewhat better fitting equations have been obtained from empirical relationships where the boiling points of particular groups of compounds are expressed as functions of several parameters for type, number and position of the constituent functional groups. These parameters, which are obtained by fitting the given equations to a number of compounds whose boiling points are known, usually are found to have none other than the

---

(6) J. Hine and S. J. Ehrenson, J. Org. Chem., 21, 819 (1956).

(7) K. Billig, Ber., 70B, 157 (1937).

(8) A. H. W. Aten, Jr., J. Chem. Phys., 5, 260 (1937).

(9) I. Prigogine and G. Garikian, J. chim. phys., 45, 273 (1948).

implied physical significance. Among many others, empirical correlation equations for normal paraffins (10), alkyl alcohols and ethers (11), alkyl mono- and dichlorides (12), group IV element hydrides (13) and alkenes (14) have been published.

---

(10) G. Rodillon, Bull. soc. chim. France, 17, 839 (1950).

(11) N. Kozlov., J. Gen. Chem. (U.S.S.R.), 20, 1059 (1950).

(12) Ibid., p. 1675.

(13) W. D. English and R. V. V. Nicholls, J. Am. Chem. Soc., 72, 2764 (1950).

(14) C. R. Kinney and W. R. Spliethoff, J. Org. Chem., 14, 71 (1949).

CHAPTER II

PROCEDURE

The Correlation Equation.--Consideration of the constant effect of substitution of one halogen for another, and also the dependence of the boiling point change upon the extent of substitution led to the following equation.

$$D = a_1X_F + a_2X_{Cl} + a_3X_{Br} + a_4X_I + \delta_{1n}X_{CH_3} + \delta_{2n}X_{CH_2} + \delta_{3n}X_{CH} \qquad (1)$$

where D is the reduced normal boiling point, the difference in boiling points between the particular halomethane and methane at one atmosphere pressure. The X's are the parameter coefficients to be determined, a_i and δ_{mn} are the parameter variables. The number of the particular halogen present is a_i (an integer between one and four; $\sum_{i=1}^{1} a_i = n$, the total number of halogens, and δ_{mn} is the Kronecker delta.[1]

Equation (1) would have the following form, for example, for dichlorobromomethane.

$$[90.1 - (- 161.4)] = 2X_{Cl} + X_{Br} + X_{CH}$$

For a given halomethane, values for the three parameter variables, δ_{mn}, uniquely express the total halogen content and imply the value of the

---

[1]For the significance and several other applications of the Kronecker delta see H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand Co., Inc., New York, N. Y., 1953, pp. 158, 325.

fourth delta (for the tetrahalomethane term). Inclusion of this dependent δ_{4n} term

$$\delta_{4n} = 1 - \sum_{m=1}^{3} \delta_{mn} \tag{2}$$

would not allow further minimization of error by the least squares method. This may be quite simply demonstrated. The equation containing the tetrahalomethane structure parameter

$$D = a_1X'_F + a_2X'_{Cl} + a_3X'_{Br} + a_4X'_I + \delta_{1n}X'_{CH_3} + \delta_{2n}X'_{CH_2} + \delta_{3n}X'_{CH} + \delta_{4n}X'_C \tag{3}$$

can be, by substitution of equation (2) and collecting coefficients with the same variable, converted to

$$D = a_1X'_F + a_2X'_{Cl} + a_3X'_{Br} + a_4X'_I + \delta_{1n}(X'_{CH_3} - X'_C) + \delta_{2n}(X'_{CH_2} - X'_C) + \delta_{3n}(X'_{CH} - X'_C) + X'_C \tag{4}$$

$$= a_1X'_F + a_2X'_{Cl} + a_3X'_{Br} + a_4X'_I + \delta_{1n}X''_{CH_3} + \delta_{2n}X''_{CH_2} + \delta_{3n}X''_{CH} + X'_C \tag{5}$$

where $X''_{CH_n} = (X'_{CH_n} - X'_C)$. Because of the mutually exclusive nature of the structure variables, equation (5) may be expressed as

$$D = a_1(X_F + \tfrac{1}{4}X'_C) + a_2(X'_{Cl} + \tfrac{1}{4}X'_C) + a_3(X'_{Br} + \tfrac{1}{4}X'_C) + a_4(X'_I + \tfrac{1}{4}X'_C) + \delta_{1n}(X''_{CH_3} + \tfrac{3}{4}X'_C) + \delta_{2n}(X''_{CH_2} + \tfrac{1}{2}X'_C) + \delta_{3n}(X''_{CH} + \tfrac{1}{4}X'_C) \tag{6}$$

Equation (6) has the same form as equation (1); only the coefficients are different.

$$X_{Hal} = X'_{Hal} + \frac{1}{4} X'_C \tag{7}$$

$$X_{CH_n} = X''_{CH_n} + \frac{n}{4} X'_C \tag{8}$$

Data Survey.--Determination of the seven parameter coefficients of equation (1) was accomplished employing a least squares treatment of all reliable boiling point data for the halomethanes available in the literature up to September, 1955. Of the 69 possible halomethanes, boiling points for 52 have been reported. Five of this group were ignored since they were either determined at a pressure considerably below 760 mm. or were for compounds reported to boil with decomposition. The data on fluorodiiodomethane was also disregarded for reasons already mentioned. Of the remaining 46 compounds, sixteen have been the subjects of considerable attention with respect to their physical properties (especially their boiling points at a number of pressures). The boiling points of these compounds were given double weight in the correlation treatment. Data on the other thirty halomethanes were cross checked when possible and the best values, as indicated by agreement of two or more independent reports, were assigned single weight. Tables 1 and 2 contain all the pertinent data to the nearest tenth of a degree, with references.

Table 1. Normal Boiling Points of the Halomethanes Assigned Double Weight in the Correlation

All values are from Timmermans (15) unless otherwise specified.

Compound	Boiling Point	Compound	Boiling Point
CH_4	-161.4°C.		
CH_3F	-78.4	$CHBr_3$	149.3
CH_3Cl	-24.1	CHF_2Cl	-40.8
CH_3Br	3.5	$CHFCl_2$	8.9
CH_3I	42.5	$CHCl_2Br$	90.1
CH_2Cl_2	40.1	CHFClBr	36.2 (17)
CH_2Br_2	97.0	CF_4	-128.0
CH_2ClBr	68.1 (16)	CCl_4	76.8
$CHCl_3$	61.7 (16)	$CFCl_3$	23.7

(15) J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 210-229.

(16) R. R. Dreisbach, Physical Properties of Chemical Substances, The Dow Chemical Co., Midland, Mich., 1953.

(17) K. L. Berry and J. M. Sturtevant, J. Am. Chem. Soc., 64, 1599 (1942).

Table 2. Normal Boiling Points of the Halomethanes Assigned Single Weight in the Correlation

Compound	Boiling Point		Compound	Boiling Point	
CH_2F_2	-51.6	(18)	CBr_4	189.5	(27)
CH_2I_2	181.0	(19)	CF_3Cl	-81.5	(28)
CH_2FCl	-8.5	(4)	CF_2Cl_2	-29.5	(4)
CH_2FBr	17.5	(4)	CF_3Br	-59.7	(29)
CH_2FI	53.4	(20)	CF_2Br_2	24.5	(30)
CH_2ClI	109.0	(21)	$CFBr_3$	107.0	(30)
CH_2BrI	139.0	(22)	CF_3I	-22.0	(4)
CHF_3	-82.2	(23)	CCl_3Br	104.1	(31)
CHF_2Br	-14.5	(23)	CCl_2Br_2[1]	135.0	(2)
$CHFBr_2$	65.0	(24)	$CClBr_3$	160.0	(2)
CHF_2I	21.0	(3,4)	CCl_3I	141.0	(32)
$CHClBr_2$	120.0	(25)	CF_2ClBr	-4.0	(4)
$CHCl_2I$	131.0	(26)	CF_2ClI	33.0	(4)
$CHFClI$	76.0	(4)	$CFCl_2Br$	51.5	(4)
$CHFBrI$	103.0	(4)	$CFClBr_2$	80.0	(4)

[1]The only boiling points recorded in the literature for dichlorodibromomethane are 135° and 150°C. An independent check at this laboratory gave 132°C. (uncorrected for pressure), lending support to the former value.

(18) A. L. Henne, ibid., 59, 1400 (1937).

(19) A. Boutlerow, Ann. chim. phys., 53, 313 (1858).

(20) A. E. Van Arkle and E. Janetzky, Rec. trav. chim., 56, 167 (1937).

(21) J. Sakurai, J. Chem. Soc., 47, 198 (1885).

(22) L. Henry, J. prakt. Chem., 32, 431 (1885).

(23) A. L. Henne, op. cit., p. 1200.

(24) F. Swarts, Bull. acad. roy. méd. Belg., 58, 113 (1910).

(25) S. Levy and K. Jedlicka, Ann., 249, 74 (1888).

(26) V. Auger, Compt. rend., 146, 1037 (1908).

(27) T. Bolas and C. E. Groves, J. Chem. Soc., 24, 780 (1871).

(28) R. Plank, Z. Eis. Kälte-Ind., 49, 77 (1942).
Chem. Zentr., 114, 69 (1943).

(29) T. J. Brice, W. H. Pearlson and J. H. Simons, J. Am. Chem. Soc., 68, 968 (1946).

(30) H. Rathsburg, Ber., 51, 669 (1918).

(31) T. E. Thorpe, J. Chem. Soc., 37, 203 (1880).

(32) W. M. Dehn, J. Am. Chem. Soc., 31, 1225 (1909).

Least Squares Treatment.--To obtain the most probable values for the parameter coefficients of equation (1) as indicated by the Gaussian law of errors, a least squares treatment of the data was employed.[1]

Taking partial derivatives with respect to each parameter coefficient (X) after rearranging, squaring and summing equation (1) over all data yields the following seven linear equations.

$$X_F \sum (a_{1j})^2 + X_{Cl} \sum a_{1j}a_{2j} + \cdots \cdots + X_{CH} \sum a_{1j}\delta_{3nj} = \sum D_j a_{1j} \qquad (9)$$

$$X_F \sum a_{2j}a_{1j} + X_{Cl} \sum (a_{2j})^2 + \cdots \cdots + X_{CH} \sum a_{2j}\delta_{3nj} = \sum D_j a_{2j}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$X_F \sum \delta_{3nj}a_{1j} + X_{Cl} \sum \delta_{3nj}a_{2j} + \cdots \cdots + X_{CH} \sum (\delta_{3nj})^2 = \sum D_j \delta_{3nj}$$

Summations, with j the running index, are over the 62 sets of data (sixteen doubly and thirty singly weighted compounds).

Computer Calculations.--The numerous arithmetic and algebraic operations necessary in determination of the seven parameter coefficients were accomplished by use of a high speed digital computer (Engineering Research Associates, model 1101).

---

[1] For a comprehensive discussion of the theory and applications of the least squares method see I. S. and E. S. Sokolnikoff, Higher Mathematics for Engineers and Physicists, 2nd. ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 521 and 536.

Two computer programs were employed, the first directed calculation of the 35 unique product summations demanded by equation (2). The second directed solution, by the computer, of the seven simultaneous equations in seven unknowns.

The values of $\underline{D}$ were calculated manually from the literature data to the nearest tenth of a degree. Rather than employ an auxiliary program to allow the computer to carry non-integer numbers, the $\underline{D}$ values were multiplied by ten. The parameter coefficient values obtained from the computer were, of course, divided by the same factor.

While the computer operations are conducted in the binary system, all instructions and data must be, for this model, furnished in octal form. The 62 sets of data were converted to this base and, along with the first program, punched out on a series of paper tapes by means of a Flexowriter typewriter-punch. The latter device was equipped with a keyboard for direct punching in the octal system. This series of tapes was then fed to the computer.

The first program (for the multiplications and summations) was composed with emphasis on the minimization of time and labor of composition rather than computer operation time. This is known as ordinary access programming. About 18 minutes of computer time was required to complete the operations dictated by this program, the results of which were stored on the electronic storage drum or "memory" of the computer. While written for this problem specifically, the capacity of this program with respect to the number of data sets to be handled and product sums to be calculated may be easily altered.

The second, a minimum access program (written to conserve machine time) was obtained from its author (33) and, with instructions on where in the "memory" to find the results of the first computations and the number of unknowns to be evaluated, was fed into the computer.[1] It directed solution of the seven simultaneous equations by a method of matrix inversion which required about five minutes of computer time. The calculations complete, the parameter coefficient values (multiplied by ten) were punched out on a tape in octal form. Conversion to printed decimal form was accomplished by feeding this tape to a Flexowriter.

---

[1]Both of these programs are contained in the Rich Electronic Computer Center library of routines as are the manuals describing operation of, and programming for, the 1101 computer. See specifically, Introduction to Programming for the 1101 Computer, PX 77000-A, Computer Applications Group, Engineering Research Associates (Division of Remington Rand, Inc.), Arlington, Va., 1953.

(33) J. C. Currie, Private communication.

CHAPTER III

RESULTS

The values obtained for the parameter coefficients are listed below to the nearest hundreth of a degree.

$X_F = 7.15$ $\quad$ $X_{CH_3} = 77.68$

$X_{Cl} = 59.06$ $\quad$ $X_{CH_2} = 85.99$

$X_{Br} = 87.15$ $\quad$ $X_{CH} = 46.79$

$X_I = 125.02$

Employing these values and equation (1), the deviations for the sets of data in Tables 1 and 2 were calculated. The sums were carried to two decimal places, followed by addition of the boiling point value for methane (- 161.37°C.) and then rounded off to the nearest tenth of a degree.

For the 16 particularly reliable compounds, the average and standard deviations are respectively 1.7 and 2.0°. For all 46 of the compounds considered, these deviations are 2.4 and 3.4°.

Four of the 46 showed deviations of more than 6.3°. These were fluoroform and methylene fluoride, respectively 10.9 and 9.5° lower than the measured values, and trifluoromethyl bromide and iodide, 6.9 and 7.1° higher than measured. In general, the four fluoromethanes as a group were predicted on the average 6.3° too low, and the halomethanes containing fluorine and one or more other halogen atoms, 2.1° too high.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The deviations between the observed and calculated values for methylene fluoride and fluoroform may be due to hydrogen bonding. Inclusion of a parameter to account for this effect probably would result in better predictions in general; this was not attempted however.

The normal boiling points of the six compounds that were not included in the calculation of the parameter coefficients for reasons previously discussed were predicted and compared to extrapolations of the reported experimental values. These data are contained in Table 3.

Table 3. Predicted and Observed Boiling Points for Some Halomethanes

Compound	Observed Temperature and Pressure	Normal Boiling Point (°C.) Extrapolated[1]	Predicted
$CHFI_2$	78° at 65 mm. (5)	147	142.6
$CHClI_2$	88° at 30 mm. (26)	196	194.5
$CHBr_2I$	101-104° at 50 mm. (26)	185-190	184.7
$CHBrI_2$	110° at 25 mm. (26)	219	222.6
CHClBrI	150° d. (34)	150	156.7
CCl_2FI	44-46 at 210 mm. (4)	80-82	88.9

[1]The enthalpy of vaporization of p-dibromobenzene has been adopted for the extrapolations for $CHClI_2$, $CHBr_2I$ and $CHBrI_2$. For CCl_2FI and $CHFI_2$, the enthalpy values of benzene and bromobenzene, respectively, were employed.

(34) M. Garino and E. Teofili, Gazz. chim. ital., 56, 847 (1926).

In light of the unstable nature of these compounds and the general extrapolative method employed (from a boiling point as a function of pressure chart, assuming the enthalpy of vaporization equal to that of a reference compound which has a similar boiling point at the reduced pressure), the agreement is quite satisfactory. For these six compounds, the average deviation between the predicted and extrapolated values is 4.5°. For only one compound, fluorodichloroiodomethane, is the deviation larger than twice the general standard deviation.

A referee of the journal publication describing this work has pointed out a parallel between the parameter values for, and the absolute boiling points of, the halogens. The equation

$$X_{Hal} = 0.317\ B.P._{Hal}\ (°K.) - 18.5°$$

may be fit with no deviation in the X_{Hal} values as great as two degrees. While the significance of this relationship is not obvious, it should hold, with a change in the intercept, if a parameter for the tetrahalomethane structure were included in the treatment.

CHAPTER V

RECOMMENDATIONS

It would be of interest to include a parameter for the tetrahalomethanes (X_C) in this type of treatment. Perhaps some recognizable relationship (recalling that obtained for the halogen parameter coefficients) would be revealed for the structure parameter coefficients.

Inclusion of a hydrogen bonding parameter has already been suggested. It would seem expedient to consider this type of bonding initially only for the fluorides.

Extension of this treatment to other haloalkanes also seems worthy of investigation, especially in light of the parallel noted between a physical property of the elemental halogens and their respective parameter values.

BIBLIOGRAPHY

General References

Margenau, H., and G. M. Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand Co., Inc., New York, N. Y., 1953, pp. 158, 325.

Sokolnikoff, I. S. and E. S., Higher Mathematics for Engineers and Physicists, 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 521 and 536.

Introduction to Programming for the 1101 Computer, PX 77000-A, Computer Applications Group, Engineering Research Associates (Division of Remington Rand, Inc.), Arlington, Va., 1953.

Literature Cited

(1) Arnhold, M., Justus Liebigs Annalen der Chemie, 240, 208 (1887).

(2) Besson, A., Comptes rendus hebdomadaries des seances de l'académie des sciences, 114, 222 (1892).

(3) Ruff, O., O. Bretschneider, W. Luchsinger, and G. Miltschitzky, Berichte der deutschen chemischen Gesellschaft, 69, 299 (1936).

(4) Haszeldine, R. N., Journal of the Chemical Society, 4259 (1952).

(5) Thomas, C. H., The Effect of Halogen Atoms upon the S_N2 Reactivity of Other Halogen Atoms Attached to the Same Carbon Atom, Part I, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1953.

(6) Hine, J., and S. J. Ehrenson, Journal of Organic Chemistry, 21, 819 (1956).

(7) Billig, K., Berichte der deutschen chemischen Gesellschaft, 70B, 157 (1937).

(8) Aten, A. H. W. Jr., Journal of Chemical Physics, 5, 260 (1937).

(9) Prigogine, I., and G. Garikian, Journal de chimie physique et Revue générale des colloides, 45, 273 (1948).

(10) Rodillon, G., Bulletin de la societé chimique de France, 17, 839 (1950).

(11) Kozlov, N., Journal of General Chemistry (U.S.S.R.), 20, 1059 (1950).

(12) Ibid., p. 1675.

(13) English, W. D., and R. V. V. Nicholls, Journal of the American Chemical Society, 72, 2764 (1950).

(14) Kinney, C. R., and W. R. Spliethoff, Journal of Organic Chemistry, 14, 71 (1949).

(15) Timmermans, J., Physico-Chemical Constants of Pure Organic Compounds, Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 210-229.

(16) Dreisbach, R. R., Physical Properties of Chemical Substances, The Dow Chemical Co., Midland, Mich., 1953.

(17) Berry, K. L., and J. M. Sturtevant, Journal of the American Chemical Society, 64, 1599 (1942).

(18) Henne, A. L., ibid., 59, 1400 (1937).

(19) Boutlerow, A., Annales de chimie et de physique, 53, 313 (1858).

(20) Van Arkle, A. E., and E. Janetzky, Recueil des travaux chimiques des Pays-Bas, 56, 167 (1937).

(21) Sakurai, J., Journal of the Chemical Society, 47, 198 (1885).

(22) Henry, L., Journal für praktische chemie, 32, 431 (1885).

(23) Henne, A. L., op. cit., p. 1200.

(24) Swarts, F., Bulletin de l'académie royale de médecine de Belgique, 58, 113 (1910).

(25) Levy, S., and K. Jedlicka, Justus Liebigs Annalen der Chemie, 249, 74 (1888).

(26) Auger, V., Comptes rendus hebdomadaires des séances de l'académie des sciences, 146, 1037 (1908).

(27) Bolas, T., and C. E. Groves, Journal of the Chemical Society, 24, 780 (1871).

(28) Plank, R., Zeitschrift für Eis-und Kälte Industrie, 49, 77 (1942). Chemisches Zentralblatt, 114, 69 (1943).

(29) Brice, T. J., W. H. Pearlson, and J. H. Simons, Journal of the American Chemical Society, 68, 968 (1946).

(30) Rathsburg, H., Berichte der deutschen chemischen Gesellschaft, 51, 669 (1918).

(31) Thorpe, T. E., Journal of the Chemical Society, 37, 203 (1880).

(32) Dehn, W. M., Journal of the American Chemical Society, 31, 1225 (1909).

(33) Currie, J. C., Private communication.

(34) Garino, M., and E. Teofili, Gazzetta chimica italiana, 56, 847 (1926).

PART III

A CORRELATION OF REACTIVITIES

IN THE BASIC SOLVOLYSIS OF HALOFORMS

CHAPTER I

INTRODUCTION

Recalling the deactivation effects accompanying substitution of one halogen atom for hydrogen in the methyl halides, it is not surprising that a second substituent halogen further decreases the S_N2 reactivity. Dichlorobromomethane, for example, is found to be less than one per cent as reactive as chlorobromomethane or methylene bromide toward iodide ion in acetone (1,2).

Toward species that are strongly basic as well as nucleophilic however, the haloforms are much more reactive than the parent methylene halides. This fact, among others, in conjunction with data on the reactions of chloroform, led Hine (3) to postulate a different mechanism for the haloform reactions. Subsequent investigations indicate that the basic hydrolysis reactions of many of the other haloforms, as well as chloroform, proceed by the alpha elimination mechanism,

$$CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O$$

$$CX_3^- \longrightarrow CX_2 + X^- \qquad \text{(rate determining)}$$

$$CX_2 \xrightarrow{OH^-, H_2O} CO + HCO_2^-$$

---

(1) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956).

(2) J. Hine, C. H. Thomas, and S. J. Ehrenson, ibid., 77, 3886 (1955).

(3) J. Hine, ibid., 72, 2438 (1950).

(where the relative amounts of carbon monoxide and formate ion formed vary with different haloforms), rather than by a rate controlling S_N2 attack by hydroxide followed by a rapid hydrolysis step (1, and references cited therein).

Because of the limited solubilities and slow rates of solution of the haloforms in water, much of the hydrolysis data had been obtained in the mixed solvent, two-thirds dioxane, one-third water (by volume). Before any correlation of the relative reactivities of the various haloforms with their structures could be properly attempted, it was desirable to have some idea of the nature of the effects of this mixed solvent upon the reactions. The rates of hydrolysis of several of the haloforms were therefore examined over a wide range of water-dioxane mixtures.

Although the generality of the alpha elimination mechanism for chloroform had been demonstrated in reactions with several alcohols and their conjugate bases (4), data was lacking on the other haloforms. Several of these were made on the subjects of kinetically studied solvolysis by methoxide in methanol. Of equal importance, these studies were intended to provide another insight into solvent effects, different from those investigations previously mentioned in that water would be absent.

Since the proposed correlation between structure and reactivity, it will be seen, depends upon the different effects exercised by the halogens contingent upon whether they are lost in the rate determining decomposition of the trihalocarbanion (as the halide ion) or remain in the dihalomethylene, knowledge of the hydrolysis rates of additional haloforms was necessary for unique separation of these effects. Every case

---

(4) J. Hine, Unpublished data.

except loss of fluoride ion in the decomposition of the trihalocarbanions, i.e., loss of chlorine, bromine and iodine as anions and presence in the dihalomethylene of all four halogens, is represented in at least one, and usually more, of the haloform hydrolysis reactions upon which data have been collected. The hydrolysis reactions of one haloform, chlorodiiodomethane, were studied for the first time, others were examined in more detail in both water and aqueous dioxane mixtures. The results of these studies and details of the correlation procedure follow.

CHAPTER II

PROCEDURE

Experimental

All the kinetic investigations were conducted in constant temperature water baths of the type described in Part I, Chapter II. Water at about 5°C. was circulated from a refrigerating unit through the cooling coils of the bath to maintain the setting at 25°C. At the higher temperature, the thermostatically controlled heaters were balanced against the heat loss to the surrounding air.

Single flask techniques were employed in all the haloform studies. In all but three runs, the haloform was weighed directly into a short-necked, nitrogen flushed volumetric flask, usually of volume 200 or 250 ml. (which contained 10 ml. of the solvent when the haloform was volatile). The flask was then cooled in an ice bath and about 100 ml. of additional solvent added. After placing the flask in the thermostatting bath, enough solvent at the temperature of reaction was added to bring the volume to within one-half ml. of the mark. The reaction was started by addition of one-half ml. of concentrated base from a hypodermic syringe; the point of the needle extended just below the surface of the solution. This was considered the zero time for the reaction. The reaction flask was then vigorously shaken and an aliquot was pipetted out within a period in which less than five per cent of base reacted. This was delivered into an erlenmeyer flask containing from fifty to eighty per cent of the standard acid necessary to neutralize the base, and about

ten grams of crushed ice. A second aliquot was taken within eight per cent of base reaction. Titration of both these samples with standard acid to the neutralization points and linear extrapolation to the starting time provided the initial base concentration.[1] At various times further aliquots or points were taken in a similar manner.

In this technique, the composition of the aqueous dioxane solvents are expressed as the ratio of the volume of dioxane to the sum of the unmixed volumes of dioxane and water. The half-ml. of aqueous base which would change these values from 0.1 to 0.2 per cent is not included.

For the reactions of chloroform in three aqueous dioxane mixtures the following procedure was employed. To the weighed sample of haloform in a 250 ml. flask was added sufficient dioxane to give the desired percentage of the total (250 ml.) volume. Fifty ml. of aqueous sodium hydroxide and enough water to reach the mark were then added at the reaction temperature.

While the partial molar volume data for this system were not available, Dowell (5) found 1.5 and 1.9 per cent shrinkages for 66 2/3 and 40 per cent dioxane solutions, respectively, at 35°C. (solutions containing base and haloform), and an abstract of the data of Tommila and Koivisto (6)

---

[1] In two reactions, bromoform and dichloroiodomethane in water at 50°C., the early points were taken after about 6 and 12 per cent of the base had reacted. The increment calculated by linear extrapolation was multiplied by the factor 1.06 which raised the initial base value by about 0.03 ml. or 0.3 per cent, an amount about equal to the titration uncertainty.

(5) A. M. Dowell, Jr., Ph. D. Thesis, Georgia Institute of Technology, 1954.

(6) E. Tommila and A. Koivisto, Suomen Kemistelehti, 21B, 18 (1948). Chem. Abs., 42, 8059d (1948).

indicates that maximum shrinkage is at 0.8 mole fraction or about 95 per cent by volume dioxane. To express the solvent composition in terms of percentage of the sum of the unmixed volumes, the following estimations have been made. Assuming a general two per cent shrinkage for the three solutions under consideration, the "mixed" composition values are multiplied by the factor 250/255 (additional two per cent or five ml. of water) to yield the corrected values. Therefore, twenty, fifty and eighty per cent dioxane (of the total volume) are 19.6, 49.0 and 78.4, respectively, dioxane (of the unmixed volumes).

Timing of the initial two points, employed in the extrapolation, was done with a stopwatch read to the nearest five seconds. If the reaction proceeded more rapidly than about 20 per cent of base consumption in 12 hours, a stopwatch read to the nearest quarter minute was employed. For the slower reactions an electric clock was read to the nearest minute. The reaction time for a given point was taken when half the aliquot volume had drained from the pipette.

As the aliquots were removed, a stream of nitrogen was played around the mouth of the reaction flask. In general, the reactions as well as the preparations were carried out under a nitrogen atmosphere.

Phenolphthalein was found to be a satisfactory indicator for the reactions in water and aqueous dioxane. The titrations in methanol were carried out with p-nitrophenol as the indicator. The latter has a pK of 7.15 (7), a useful indicator range of 5 to 7 in the same solvent (8), and a basic yellow color (colorless in acid). While the pK value in methanol

---

(7) R. G. Bates and G. Schwarzenbach, Helv. Chim. Acta, 37, 1069 (1954).

(8) Handbook of Chemistry and Physics, 30th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1947, p. 1402.

is not available, it is known for absolute (9), and 30 per cent aqueous (10), ethanol (10.1 and 7.7 respectively). Kolthoff and Guss (11) have measured the ionization constants of several weak, uncharged acids in absolute methanol and found the pK values to be on the average 4 to 5 units higher than in water. Since, in the titrations under consideration, the methanol concentration at the neutralization point was about 60 per cent, and pK's generally appear to increase more rapidly in the more strongly alcoholic solutions, a pertinent pK value of about 9 is suggested. Examination of the properties of this indicator in water suggests a useful pH range of about 7 to 9.

Standard aqueous hydrochloric acid was used to titrate many of the runs. This acid was unsatisfactory, however, if halide ion was to be determined from the same aliquot. Titration with standard perchloric acid to the neutral point was followed by addition of chromate and titration with standard nitrate for halide by the Mohr method. From these data, f values (fraction of haloform hydrolyzed which gives formate) could be calculated from the equation

$$f = 3\left(\frac{\Delta[OH^-]_t}{[X^-]} - 1\right) \qquad (1)$$

since three moles of base are consumed by haloform in formation of a mole of carbon monoxide and four moles of base are required per mole of formate ion formed.

---

(9) W. D. Treadwell and G. Schwarzenbach, Helv. Chim. Acta, 11, 386 (1928).

(10) R. A. Benkeser and H. R. Krysiak, J. Am. Chem. Soc., 75, 2421 (1953).

(11) I. M. Kolthoff and L. S. Guss, ibid., 60, 2516 (1938).

Preparation and Purification of Reagents

The methods of purification employed for methanol and of preparation of sodium methoxide have been described in Part I, Chapter II.

Water.--Distilled water was either boiled and stored under nitrogen or treated with bubbling nitrogen for an hour or more prior to use.

Dioxane.--Commercial dioxane was purified by the method of Fieser (12), distilled under nitrogen and stored in a brown bottle over sodium wire.

Chloroform.--About 500 ml. of a previously purified sample of chloroform was redistilled and stored in a brown bottle under nitrogen. The boiling point was 61.2°C. Prior to use, a stream of nitrogen was blown through the product to remove any phosgene and hydrogen chloride present.

Dichlorobromomethane, Chlorodibromomethane and Bromoform.--Small samples of these haloforms which had been purified and stored in sealed glass ampules were obtained from Dr. J. Hine and used without further purification.

Dichloroiodomethane.--A sample of dichloroiodomethane, prepared and purified by Dr. A. M. Dowell and stored at zero degrees, was treated with Drierite and employed. The liquid was colorless.

Chlorodiiodomethane.--Chlorodiiodomethane was prepared by the method of Auger (13) by heating an intimate mixture of 312 grams of iodoform and 100 grams of mercuric chloride under a partial vacuum (35 to 60 mm.). The distillation head temperature ranged from 85 to 110°C. About 50 ml. of a deep red liquid was collected and fractionated in the dark under

---

(12) L. F. Fieser, Experiments in Organic Chemistry, Part II, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(13) V. Auger, Compt. rend., 146, 1037 (1908).

nitrogen in a Todd still. Three cuts were made, about 35 ml. of the desired product being obtained over the range 98 to 104°C. at a pressure of 32 mm. After washing with aqueous sodium thiosulfate and water, the product was redistilled; the yield was about 30 ml. at 101-2°C. at 33 mm. The product quickly assumed a reddish tinge in the presence of light. Therefore, prior to use the samples were washed with thiosulfate and several portions of water and dried over Drierite.

Sodium Hydroxide Solutions.--Concentrated sodium hydroxide solutions (4 to 6 N.) were prepared by dissolving weighed quantities of the base in distilled water within a polyethylene bottle and were stored therein under nitrogen.

Hydrochloric and Perchloric Acid Solutions.--Samples of the concentrated acids were diluted with distilled water. Solutions of the former were standardized against aqueous base with phenolphthalein. The latter acid solutions were prepared from primary standard samples in sealed ampules and therefore required no standardization.

CHAPTER III

RESULTS

In general, for the haloforms studied, the rate constants for basic solvolysis were calculated from the integrated rate equation[1]

$$k = \frac{2.303}{t[(3 + f)a_o - b_o]} \log \left(\frac{b_o}{(3 + f)a_o} \right) \frac{b + [(3 + f)a_o - b_o]}{b} \qquad (2)$$

where $\underline{a}_o = [CHX_3]_o$, $\underline{b}_o = [\text{base}]_o$, $\underline{b} = [\text{base}]_t$ and $\underline{t}$ = time. The significance and means of determination of $\underline{f}$ have previously been discussed. For a particular haloform undergoing hydrolysis its value lies between zero and unity, depending upon the ratio of formate ion to carbon monoxide produced as final products. In the methanolysis reactions its only value is zero; the two final products, carbon monoxide and methyl orthoformate, both require three moles of base in formation from the haloform.

Since the temperature and presence of dioxane do not appear to affect the $\underline{f}$ values for the particular haloform hydrolysis reactions noticeably (5, 14), and recognizing that these values should be the same for all haloforms yielding the same dihalomethylene intermediate, the values of $\underline{f}$ for hydrolysis of all but two of the haloforms studies were available or estimable from the results of previous investigations conducted in this laboratory.

---

[1] For the derivation of this equation, see reference (3).

(14) J. E. Singley, Jr., M. S. Thesis, Georgia Institute of Technology, 1952.

An attempt to determine f for chlorodiiodomethane (reaction in pure water at 50°C.) was unsuccessful; wide variations and negative values were obtained. The data are contained in Table 33. In two-thirds dioxane at 50°C. however, the somewhat better values reproduced in the fourth column of Table 1 were obtained. While the variations are sufficient to preclude confident acceptance of any one of these values or their average, the observation that f is smaller for the dihalomethylenes containing heavier halogens is supported. The rate constant calculations for the chloroiiodomethane reactions have been made, employing equation (2), assuming f equal to zero.

Several attempts by Singley (14) to measure the f value for bromoform gave widely varying results (0.13 to 0.23). It was recognized that f is extremely sensitive to side reactions, e.g., oxidation or the presence of impurities (especially when the true value is small; see equation (2)). Also, the values obtained seemed too high, judging by the observation that heavier halogens in the dihalomethylene result in lower f values. A redetermination was made, the results of which appear in Table 35, with no better success as far as constancy is concerned. The values however do appear to be somewhat smaller. In the absence of a precise value, 0.08 (approximately the same as that for dibromochloromethane) was chosen for the hydrolysis reactions of bromoform.

Reproduced in Table 2 are the rate constants for hydrolysis of the three haloforms studied extensively in varying aqueous dioxane media. In Table 3 are to be found the hydrolysis constants in water and in two-thirds dioxane (other than those presented in Table 2), and the rate constants for methanolysis. Included in these tables are references to the

Table 1. $CHClI_2$ + NaOH in Two-Thirds Aqueous Dioxane at 50°C.

$CHClI_2$ 0.008643 M — $HClO_4$ 0.0493 M

NaOH 0.01580 M — $AgNO_3$ 0.0596 M

25 ml. samples

Time in Seconds	ml. of $HClO_4$	ml. of $AgNO_3$	(f)	10^4k (l./m.s.)
0	9.65[1]	-		-
155	9.57	-		-
345	9.48	-		-
1730	8.91	0.53	(-0.123)	18.16
3705	8.19	1.00	(0.010)	17.92
6590	7.34	1.58	(0.012)	17.35
11310	6.17	2.35	(0.051)	17.39
14520	5.52	2.83	(0.028)	17.43
18310	4.77			18.13

[1]By extrapolation. f = 0.00, see page 78.

Average k = (17.73 ± 0.34) x 10^{-4} l./m.s.

Table 2. Haloform Hydrolysis Rates in Aqueous Dioxane at 35°C.

Compound	10^4k (l./m.s.) (volume per cent dioxane)	
$CHCl_3$[2]	3.00 ± .04 (19.6)[1],	3.48 ± .05 (49)[1]
	3.42 ± .07 (60),	3.01 ± .03 (66.7)
	3.45 ± .06 (72),	4.24 ± .08 (78.4)[1]
$CHCl_2Br$[2]	65.6 ± 0.8 (29.4),	70.6 ± 1.1 (40)
	80.7 ± 1.3 (50),	76.8 ± 1.2 (60)
	83.8 ± 1.2 (66.7),	86.0 ± 0.7 (75)
$CHBr_3$[3]	11.0 ± 0.1 (36.4),	11.6 ± 0.1 (50)
	12.1 ± 0.1 (66.7)	

[1]Corrected values for solvent composition, see Chapter II.

[2]f = 0.15, see reference (5).

[3]f = 0.08, see page 78.

Table 3. Haloform Hydrolysis Rates in Water (W), Two-Thirds Aqueous Dioxane (D) and Rates of Methanolysis (M)

Compound		10^4k (l./m.s.) 25°C.	50°C.
$CHCl_3$	(M)		0.306 ± 0.004
$CHCl_2Br$ [1]	(W)		307 ± 24 [7]
	(M)		9.25 ± .05
$CHClBr_2$ [2]	(W)		220 ± 13 [7]
	(M)		6.30 ± .07
$CHBr_3$ [3, 5]	(W)	1.99 ± .03	83.8 ± 3.4 [7]
$CHCl_2I$ [1]	(W)	2.17 ± .03	95.2 ± 5.8 [7]
$CHClI_2$ [4]	(W)	112 ± 25 [6, 7]	9.21 ± .29 [7]
	(D)	179 ± 9 [6, 7]	17.7 ± 0.3

[1] f = 0.15, see reference (5).

[2] f = 0.083, see reference (5).

[3] f = 0.08, see page 78.

[4] f = 0.00, see page 78.

[5] At 35°C., 10^4k = 9.54 ± .14.

[6] At 67.1°C.

[7] These values have been obtained graphically; details of the method follow.

source from which the particular values of f were adopted. The experimental data and individual rate constants for the points are to be found in tabulated form in the Appendix. Within the individual runs, points taken before eight minutes and/or five per cent reaction and after 85 per cent reaction of the base were not used to calculate rate constants.

For several of the haloforms, solvolysis data obtained at the higher temperatures (50°C. and above) yielded rate constants, calculated from equation (2), that fell slightly as the reaction proceeded. Several re-runs indicated that experimental errors were not responsible for the effect.

It was noted that plots of the logarithm factors, from the right side of equation (2), against time could usually be fit quite well by a straight line, especially if the last one or two points, taken late in the reaction, were ignored. In most cases, the ordinate intercept (time equal zero) was noticeably positive.

Of the readily apparent hypotheses that would account for the graphical linearity and non-zero intercepts, one, which assumes a timing error, is totally unsatisfactory. It is true that addition of the number of time units represented by the distance in the plots from the origin to the abscissa intercept to the reaction time for each point would yield essentially constant rate constants. However, for most of the runs this quantity is on the order of two minutes or more which, in the light of the reaction timing procedures, is quite unreasonable.

Another hypothesis which appears much more reasonable assumes a highly reactive impurity in the haloform sample. This assumption requires the initial haloform concentration employed in equation (2) to be

in error (too high). There are several possibilities concerning the concentration of base.

If the impurity is so reactive that it has consumed base and disappeared before the two early aliquots are taken, the extrapolated initial concentration of base will be that which actually reacts with the haloform. If the impurity persists, however, and continues to react while one or both of the two early points, employed in the extrapolation to obtain the initial base concentration, are taken, the extrapolated value will be larger than the amount that reacts with haloform (since some reacts with impurity). Because the most likely impurities are the phosgenes or carbonyl halides and the hydrogen halides (arising from the oxidation of the haloforms), it is doubtful that consumption of base in the side reaction would still be going on by the time the first point yielding a rate constant is taken.[1]

For the first case (where only the initial haloform concentration is in error) the true rate constants will be larger than any calculated from equation (2). For small amounts of impurity the log factor versus time plot might appear linear over a short range since, it may be shown that,

$$\frac{\text{slope } (t = 0)}{\text{slope } (t = \infty)} = \frac{(3 + f)a'_o - b_o a'_o/a_o}{(3 + f)a'_o - b_o} \qquad (3)$$

---

[1] Phosgene undergoes solvolysis with water and alcohols; replacement of the second chlorine is relatively slow with alcohols (15, 16). Base appears to accelerate the reactions and is occasionally used in further esterification of the chlorocarbonic esters (Schotten-Baumann method).

(15) R. Leimu, Ber., 70B, 1040 (1937).

(16) P. Karrer, Organic Chemistry, Elseiver Publishing Co., Inc., New York, N. Y., 1950, p. 228.

and,

$$\text{slope } (t = 0) = \left(\frac{a'_o}{a_o}\right) k \frac{(3 + f)a_o - b_o}{2.303} \qquad (4)$$

where a'_o and a_o are the true and assumed initial haloform concentrations respectively. However, trial corrections for the haloform concentrations in several sets of data to an impurity level of 15 per cent (in increments of 3 per cent) failed to substantially improve the constancy of the rate constants within the given runs.

If both the initial haloform and base concentrations are in error, assuming the impurities are as postulated, the correct picture lies somewhere between the above and the one which has the impurity reacting the same as the haloform stoichiometrically but faster (maximum error for base is then 3 + f times that for haloform). For the latter case which is a limiting condition and probably unrealistic, the rate constants would be smaller than any calculated from equation (2) (except those represented by points lying well below the straight line) and the log factor versus time plot would be linear with positive intercept and

$$\text{slope} = k \frac{(3 + f)a_o - b_o}{2.303} \qquad (5)$$

It is of interest to note that employment of this limiting assumption would have, in effect, the same result as that forthcoming from the shift in the time axis mentioned previously.

In absence of exact information concerning the presence, nature and reactivity of the impurities preventing any more pertinent analysis, the latter method of calculation (equation (5)) for the rate constants

in question has been chosen. Figure 1, reproduced below, is the log function versus time plot for the hydrolysis reaction of chlorodibromomethane in pure water at 50°C. (data contained in Table 4), and is used to illustrate the graphical estimation method described. The data for the other runs in question (superscript seven in Table 3) appear in the Appendix.

The uncertainties attached to the values obtained graphically have been arbitrarily set equal to the difference between the graphical value and the average of the calculated values or the mean deviation of the average values, whichever quantity is larger.

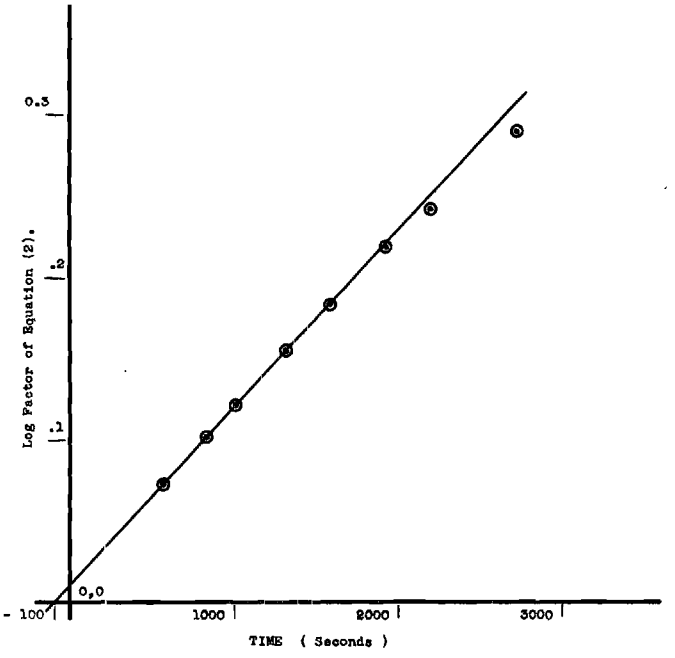


Fig. 1. Log Factor of Equation (2) versus Time for $CHClBr_2$ + NaOH in Water at 50°C.

Table 4. $CHClBr_2$ + NaOH in Water at 50°C.

$CHClBr_2$ 0.008937 M $HClO_4$ 0.04028 M

NaOH 0.01618 M 20 ml. samples

Time in Seconds	ml. of $HClO_4$	Log Function	$10^4 k$ (l./m.s.)
0	7.84	-	-
80	7.47	-	-
195	6.94	-	-
580	5.47	0.0714	249.3
847	4.78	.1017	243.2
1025	4.41	.1209	239.0
1325	3.86	.1538	235.2
1595	3.46	.1826	231.9
1925	3.04	.2176	229.0
2200	2.80	.2412	222.1
2730	2.38	.2894	214.7

f = 0.083

Average k = (233.1 ± 8.6) x 10^{-4} l./m.s.

Graphical k = (220 ± 13) x 10^{-4} l./m.s.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The primary intention of this phase of study was to determine how satisfactory a correlation, consistent with the accepted mechanism, could be found between the relative rates of the basic solvolysis reactions of the haloforms and their structures. The correlation method is presented in detail immediately below and thereby serves as an appropriate framework within which to discuss the experimental results.

The Correlation Equation

As noted previously, many of the haloforms undergo hydrolysis by the mechanism[1]

$$CHXYZ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CXYZ^- + H_2O$$

$$CXYZ^- \xrightarrow{k_2} CXY + Z^-$$

whereupon the carbon dihalide rapidly reacts to give formate and/or carbon monoxide. The rate constant for hydrolysis, (k_h), calculated from experimental data by means of equation (2), is

---

[1]Of the 20 possible haloforms, 16 are expected to undergo hydrolysis by the alpha elimination mechanism. The remaining three, besides fluoroform which hydrolyzes too slowly to be measured, (the chloro-, bromo- and iodo- difluoromethanes) are felt to hydrolyze by a concerted mechanism. i.e., where the proton and halide ion are lost simultaneously to yield difluoromethylene.

$$k_h = \frac{k_1 k_2}{k_{-1} + k_2} = \frac{k_1(k_2/k_{-1})}{1 + (k_2/k_{-1})} \qquad (6)$$

The values of k_1 have been ascertained by Hine, et. al. (14, 15) for some of the haloforms, and may be estimated for the others from the data of these workers in a manner presently to be described. Therefore, correlation of the rate constant ratio (k_2/k_{-1}) with haloform structure in effect provides a relationship between the latter and the rates of hydrolysis.

The ratio (k_2/k_{-1}) is simply the rate constant for formation of the dihalomethylene from the trihalocarbanion divided by the rate constant for recombination of this trihalocarbanion with protons from water to yield the haloform. Three factors have been assumed to control the relative values of k_2; one relates to the ease of departure of the halide ion (Z^-, above) in the transition state for formation of the dihalomethylene. The second depends upon the stabilization abilities of the halogens (X and Y) which remain attached to the dihalomethylene in the product. The third factor concerns the stabilization effects of the three halogens upon the carbanion structure.

Factor one, concerned with the ease of departure of Z^-, might be expected to exhibit the order, $I \approx Br > Cl > F$, in light of the behavior of known organic halides undergoing halide ion loss. The order of decreasing stabilization by the remaining halogens to the dihalomethylene structure may be, $F > Cl > Br > I$, since resonance forms of the type

---

(17) J. Hine and N. W. Burske, J. Am. Chem. Soc., 78, 3337 (1956).

(18) J. Hine, N W. Burske, M. Hine and P. B. Langford, ibid, In press.

$$Y - C^{+} = X^{-} \qquad Y - \ddot{C} - X \qquad Y - \ddot{C}^{-} = X^{+}$$

I II III

are to be expected. The participation of fluorine in π bond structures (i.e., III) through donation of its own electrons (recalling the discussion of Part I, Chapter IV) should be stronger than that of the less electronegative halogens. Acceptance of the unshared pair from carbon, structure I (d-orbital resonance), however should be more difficult for fluorine than for the other halogens. That structures of type III are probably more important than I is suggested by the electrophilic rather than nucleophilic behavior of the carbon dihalides demonstrated in combination studies with halide ions (19). For the third factor, substituents which tend to stabilize the carbanions will decrease k_2. Preliminary prediction of the order of carbanion stabilization is difficult. While induction and d-orbital resonance by the halogen might be expected to stabilize, π bond formation by electron donation from the halogen would likely destabilize the carbanion.

The assumption has been made that the factors controlling carbanion stabilization are adequately measured by k_1 (the rate constant for carbanion formation from haloform). Therefore, with the further assumption that the effects of all the factors mentioned are linear with respect to the free energy of activation, we arrive at the equation

$$\log k_2 = \sum_{X,Y} M + N_Z + \log n - a \log k_1 + \text{constant} \qquad (7)$$

---

(19) J. Hine and A. M. Dowell, Jr., ibid., 76, 2688 (1954).

The sum of the methylene stabilization factors for the two halogens (X and Y) is $\sum_{X,Y} M$, N_Z is a constant for the halogen (Z) being lost as an anion in the transition state, log n is a statistical factor where n is the number of halogens (Z), and a is a proportionality constant, assumed to be the same for all haloforms. The latter constant may be thought of as the fractional change in carbanion character between the trihalocarbanion and transition state in dihalomethylene formation divided by the fractional change in carbanion character between the haloform and transition state in carbanion formation. The remaining factors contributing to k_2 are assumed equal for all the haloforms considered under the particular conditions (solvent composition, temperature, etc.) and are grouped together into the constant last term of equation (7).

From the Brønsted catalysis law it is gathered that acids that donate protons most rapidly are usually those whose conjugate bases accept protons the slowest. While the number of exceptions to this generalization are considerable (20), we shall assume it holds for the haloforms acting as acids, particularly since they form a series of closely related compounds and their acid-base reactions should not be complicated by such factors as internal rotation and steric inhibition of resonance. Putting this generalization in quantitative form

$$\log k_{-1} = -b \log k_1 + \text{constant} \qquad (8)$$

where b is a proportionality constant having a meaning analogous to that of a and the constant is similar in meaning to the last term of equation (7).

---

(20) R. G. Pearson and R. L. Dillon, ibid., 75, 2439 (1953).

Combining equations (7) and (8) yields

$$\log (k_2/k_{-1}) = \sum_{X,Y} M + N_Z + \log n + (b - a) \log k_1 + \text{constant} \quad (9)$$

Since we are discussing relative reactivities, it is only the relative magnitudes of the M and N parameters that are significant. Therefore, their absolute values may be assigned arbitrarily. We have done so by setting M_{Cl} and N_{Cl} equal to zero. That is, the reactions shall be discussed relative to chloroform as the standard. For chloroform equation (9) has the form

$$\log (k_2/k_{-1})_{CHCl_3} = \log 3 + (b - a) \log k_1^{CHCl_3} + \text{constant}$$

Combination with the appropriate form of equation (9) for another haloform, CHXYZ, and recognition that equation (6) may be expressed as

$$k_2/k_{-1} = k_h/(k_1 - k_h), \text{ yields}$$

$$\log \frac{k_h/(k_1 - k_h)_{CHXYZ}}{k_h/(k_1 - k_h)_{CHCl_3}} = \sum_{X,Y} M + N_Z + \log (n/3) + (b - a) \log \frac{k_1^{CHXYZ}}{k_1^{CHCl_3}} \quad (10)$$

which is the final and employed form of the correlation equation.

Hydrolysis Reactions in Pure Aqueous Solution

Listed in Table 5 are the rate constants for basic hydrolysis (k_h) and for proton removal by hydroxide (k_1) obtained for the haloforms studied in aqueous solution at zero degrees. Since more rate studies had been conducted at this than at any other single temperature, it was chosen as a condition for comparison of the reactivities. In fact, all the haloforms to be included in this correlation with the exception of those investigated by the author had been studied at this temperature. The slow rates of hydrolysis in water and the unstable natures with respect to oxidation of bromoform, dichloroiodo- and chlorodiiodomethane discouraged direct examination at zero degrees. Extrapolation by means of Arrhenius rate equation plots (log k_h versus $1/T$, data from Table 3) yielded the values for these three haloforms contained within parentheses in Table 5. A k_h value of 11.6×10^{-4} l./m.s. at 35°C. for dichloroiodomethane was obtained by the discussed graphical treatment of the data of Dowell (5) and was employed in the extrapolation at zero degrees.

For fluorodichloro-, fluorodibromo- and fluorochlorobromomethane, haloforms which undergo hydrolysis at a rate comparable to the removal of protons, values of k_1 had been obtained in the manner described in reference (17). For all the rest of the haloforms in aqueous solution, except chlorodiiodomethane, these constants were calculated from the observed rates of hydroxide ion removal of deuterium from the deuterohaloforms through multiplication by the isotope effect factor.[1]

---

[1]The isotopes effects for the reactions of three haloforms have been measured and found to be within experimental error (four per cent) of each other. At zero degrees, fluorodichloro- and fluorochlorobromomethane have the isotope reactivity ratios 1.76 and 1.75 respectively. At twenty degrees, the values for chloroform and fluorodichloromethane are respectively 1.48 and 1.52. It has therefore been assumed that an isotope effect of 1.75 holds generally for all the haloforms considered at zero degrees.

Table 5. Kinetic Constants for the Basic Hydrolysis of, and the Proton Removal from, Haloforms in Aqueous Solution at Zero Degrees

Compound	$10^4 k_h$ (l./m.s.)		k_1 (l./m.s.)	
$CHCl_3$	0.00602 ± 0.00039	(5)	0.0082 ± 0.0002	(21)
$CHBr_3$	(0.0241) [1]		1.02 ± 0.01	(18)
$CHClBr_2$	0.0665 ± 0.002	(23)	0.250 ± 0.004	(18)
$CHCl_2Br$	0.149 ± 0.019	(23)	0.051	(22)
$CHFCl_2$	0.123 ± 0.001	(17)	$0.000157 \pm 0.0_503$	(17)
$CHFBr_2$	28 ± 1	(24)	0.031 ± 0.002	(23)
$CHFClBr$	13.2 ± 0.2	(18)	$0.00355 \pm 0.0_408$	(18)
$CHClI_2$	(0.000764) [1]		(0.23) [2]	
$CHCl_2I$	(0.0216) [1]		0.0467 ± 0.0007	(18)
$CHFI_2$	1.530 ± 0.025	(23)	0.089 ± 0.004	(23)

[1] Obtained by extrapolation from higher temperatures.

[2] Estimated as explained below.

(21) J. Hine, R. C. Peek, Jr., and D. B. Oakes, ibid., 76, 827 (1954).

(22) R. C. Peek, Jr., Unpublished data from a single point.

(23) J. Hine and P. B. Langford, Unpublished data.

(24) R. Butterworth, M. S. Thesis, Georgia Institute of Technology, 1956.

Examination of Table 5 reveals that the rates of proton removal by hydroxide may be satisfactorily fit to the equation

$$\log (k_1)_{CHX_{3-n}Y_n} = \log (k_1)_{CHX_3} + n\, C_Y \qquad (11)$$

where C_Y is a constant. For the chlorine, bromine containing haloforms, the values of C_{Br} are 0.79, 0.74 and 0.70, respectively, for the mono-, di- and tribromo compounds compared to chloroform. The known k_1 values for the chlorine, iodine containing haloforms yield C_I values of 0.75 and 0.70, respectively, for the mono- and triiodo compounds compared to chloroform. Since the value of C_{Br} for the dibromo haloform is approximately the algebraic mean of the values for the mono-and tribromo compounds, a C_I value of 0.72 has been adopted for chlorodiiodomethane and the k_1 value (0.23 l./m.s.) obtained from equation (11).

By inspection and successive approximations the following parameter coefficient values were obtained.[1]

$M_F = 3.95$	$N_{Br} = 0.65$
$M_{Br} = -1.60$	$N_I = -0.10$
$M_I = -2.80$	$(b-a) = 0.5$

When substituted appropriately in equation (10), $\log [k_h/(k_1 - k_h)]$ values are obtained which have an average deviation of 0.04, corresponding to an uncertainty of less than 10 per cent in $[k_h/(k_1 - k_h)]$. Since the

---

[1] At least one (chlorobromoiodomethane) and probably more haloforms are to be studied and included within this correlation. Therefore, a more exact treatment of data fitting, e.g., least squares, was not undertaken.

uncertainties of the k_h and k_l values determined at zero degrees are on the average about four per cent, and recalling the approximative methods for estimation of several of these constants, the agreement between the calculated and experimental values is quite satisfactory.

That b is larger than a suggests that the trihalomethyl anions lose more carbanion character in the transition state of their transformation to haloform than they do in the transition state of their decomposition to dihalomethylenes. This does not seem unreasonable, particularly in view of the considerable carbanion character of the dihalomethylene which has an unshared electron pair in what is probably the principle contributing structure, i.e., X - $\ddot{C}$ - Y.

The halogen stabilization factors, M, for the dihalomethylene transition state structure are in the order, F > Cl > Br > I. It does not seem unreasonable that the same order would hold for the dihalomethylenes. As previously speculated, this order likely arises from the contribution of structures with carbon-halogen double bonds, primarily formed by electron donation from the halogen with some participation of d-orbital resonance forms where halogen accepts the unshared electron pair from carbon.

The parameter values, N, which represent the ease of departure of halide ions in the transition state (between the trihalocarbanion and dihalomethylene) did not agree with expectation. For example, the value of N_{Br} (0.65) indicates that bromide is only between four and five fold more easily lost than chloride, considerably smaller than the usual solvolysis reactivity differences noted; (compare with the tabulated S_N1

reactivities of organic halides by Streitwieser (25)).[1] Even more surprising is the value of the parameter for iodine (-0.10) which signifies that iodide ion is liberated less readily than chloride. The unreactive nature of fluoroform ($k_h < 10^{-6}$ at 50°C.) suggests that N_F has a large negative value, which is as expected.

While N_I is slightly smaller than N_{Cl}, granting that differences of a tenth of a unit are significant in a correlation method based upon assumptions calculated to lead to a simple rather than complexly rigorous equation, this does not mean that a haloform containing iodine and chlorine will lose the latter more readily in formation of the dihalomethylene. Examination of the parameter coefficient values immediately reveals the loss in dihalomethylene stabilization upon loss of chlorine rather than iodine from the carbanion would more than make up for the slight gain arising from the N value difference. The value of k_h may be calculated from equation (10) for chloroiiodomethane, for example, for chlorine loss in the rate determining step. Here $2M_I$, n (equal one) and k_1 equal 0.23 l./m.s. (from Table 5) must be included; k_h equal 7.4×10^{-11} l./m.s., which is about a thousand times smaller than the hydrolysis constant when iodide ion is lost in the rate determining step. As equation (10) reveals, the N values are of significance alone only for comparisons drawn between haloforms yielding the same dihalomethylene.

---

[1] It should be noted that comparisons drawn with the S_N1 reactivities of organic halides should not be overemphasized since halogen displacements in the cases under discussion are from negatively charged species, the trihalocarbanions.

(25) A. Streitwieser, Jr., Chem. Revs., 56, 654 (1956).

Hydrolysis Reactions in Aqueous Dioxane

Table 6 contains the k_h values for seven of the haloforms whose hydrolysis reactions were studied in two-thirds dioxane solution. The data is given at 35°C., a temperature at, or near, which most of the reactions were run. For those haloforms studied at other temperatures, extrapolation or interpolation by Arrhenius plots yielded the values contained within parentheses in Table 6. The k_h value for chlorodibromomethane was obtained by interpolation of the data of Hine, et. al. (1) at zero, 25.3 and 35.7°C. The extrapolations were made on the data for iodoform at 50 and 70.4°C. ($10^4 k_h$ equals 7.2 ± 0.8 and 170.5 ± 4.1 l./m.s., respectively) (23), and on those obtained by the author from Tables 22 and 23.

Since the presence of dioxane precludes direct measurement of k_1 by the method employed for the reactions in aqueous solution,[1] these constants were estimated assuming equation (11) holds in this solvent, as it appears to have held in pure aqueous solution. Substituting equation (11), where CHX_3 is chloroform (again the standard of comparison) and Y is bromine or iodine, into equation (10) yields

$$\log \frac{\left[k_h/(k_1-k_h)\right]_{CHCl_{3-n}Y_n}}{k_h/(k_1-k_h)_{CHCl_3}} = \sum M + N_Y + \log \left(\frac{n}{3}\right) + n\,(b-a)\,C_Y \qquad (12)$$

---

[1] The value of k_1 is calculated from the rate of isotopic exchange which is followed experimentally by extraction of the reaction solution with carbon disulfide or isooctane to remove the haloform and measurement of the deuterium content therein by I. R. spectroscopic examination. Full details of the procedure are to be found in references (17, 18 and 21).

$$= (n-1)M_Y + N_Y + \log\left(\frac{n}{3}\right) + n\,(b-a)\,C_Y \qquad (13)^1$$

Examination of Table 5 reveals that only for the fluorine-containing haloforms was k_1 noticeably different from (k_1-k_h). Assuming that this observation may be carried over for the reactions in the dioxane-containing-solvent (i.e., for the haloforms considered in two-thirds aqueous dioxane, let k_1 equal (k_1-k_h), the left side of equation (13) becomes, upon substitution of equation (11),

$$\log \frac{(k_h/k_1)_{CHCl_{3-n}Y_n}}{(k_h/k_1)_{CHCl_3}} = \log \frac{(k_h)_{CHCl_{3-n}Y_n}}{(k_h)_{CHCl_3}} - nC_Y \qquad (14)$$

Inserting equation (14) into equation (13) and rearranging yields

$$\log \frac{(k_h)_{CHCl_{3-n}Y_n}}{(k_h)_{CHCl_3}} = \log \frac{n}{3} + n[C_Y(1+b-a) + M_Y] + [N_Y - M_Y] \qquad (15)$$

For the chlorine, bromine haloforms three data are available to be fit to two unknowns (in brackets in equation (15)). This is also the case for the chlorine, iodine haloforms.[2] Arbitrarily choosing the data for the mono- and tri- bromides and iodides, values for the di- compounds were calculated and are to be found in Table 6. The values of

---

[1] Since only chlorobromides and chloroiodides are considered, $\sum_Y M = (n-1)M_Y$.

[2] Explicit evaluation of unknowns M_Y, N_Y and $C_Y(1+b-a)$ is impossible since the simultaneous equations (two sets of three equations in three unknowns) are integer multiples of the primatives, $(n-1)M_Y + (n)C_Y(1+b-a) + N_Y$, with n the integer.

$[C_Y(1+b-a) + M_Y]$ and $[N_Y - M_Y]$ for the chlorine, bromine haloforms are, respectively, -0.659 and 2.581. For the chlorine, iodine haloforms these parameters are -1.172 and 2.772. If agreement between the predicted and observed values of k_h is a sufficient criterion of the applicability of the method, it is apparent that the bromides are fit successfully. The iodides, however, exhibit an appreciable deviation (the predicted value is about three times as large as the observed k_h value for chlorodiiodomethane).

Which one, or more, of the chlorine, iodine haloforms is responsible for the poor fit of the correlation is not obvious; however, iodoform is deserving of considerable scrutiny for several reasons. Going from pure water at zero degrees to two-thirds dioxane at 35°C., the k_h values for the chlorine, bromine compounds are all increased by essentially a constant factor (530 ± 30 fold). The mono- and di- iodo compounds are hydrolyzed respectively about 1900 and 2300 times as fast, again a reasonably constant effect. The effect upon iodoform (k_h equal about 1.7×10^{-9} l./m.s. at zero degrees in pure water; calculated from the parameter values presented, with k_1 equal to 1.05 l./m.s. (15)) is about a 32,000 fold increase, about 14 times that noted for chlorodiiodomethane. If k_h for iodoform in two-thirds dioxane at 35°C. were a twelfth as large as the observed value, both the constancy in effect upon the rate of hydrolysis accompanying the discussed change of solvent and temperature (about 2700 fold acceleration) and fit to the correlation in dioxane (predicted value for chlorodiiodomethane of about 1.6×10^{-4} l./m.s.) would be forthcoming. Of course, these calculations are based upon the presumption that iodoform will be adaptable to the proposed correlation in aqueous solution at zero degrees. The fact that of the seven

haloforms examined in dioxane, all were found to fit the correlation in water at zero degrees, with the exception of iodoform (which was not examined in aqueous solution) also indicates that the latter may be responsible for the variations noted. Why iodoform should exhibit such deviations in dioxane and, perhaps in aqueous solutions is, however, not apparent.[1, 2]

An attempt was also made to gain some insight into the effects of dioxane upon the rates of hydrolysis of the haloforms by varying the composition of the solvent over a wide range. The three haloforms, chloroform, dichlorobromomethane and bromoform, were examined in some detail in several dioxane-water mixtures at 35°C.; the relative rates of

---

[1] It is of interest to note that the reactions of iodoform with the bases, sodium ethoxide and isobutoxide, are reported to give a number of unusual products. Arising from reactions with the former are methylene iodide, α-methoxypropionic acid and acrylic acid (26). With isobutoxide, the products are, formic, isobutyric, β,β-dimethylacrylic and α-isobutoxyisobutyric acids, another acid with the formula $C_8H_{16}O_3$, methyl isobutyl ether, diisobutoxy methylene, isobutylene and the compound, $(CH_3)_2C(OC_4H_9)CH(OH)OC_4H_9$ (27).

[2] An estimation of the S_N2 reactivity of iodoform is possible. Toward methoxide ion in methanol, substitution of iodine for hydrogen in methyl iodide causes a 400 fold decrease in S_N2 reactivity at 50°C. (10^5k, from 433 to 1.07) (2). Since the deactivation effect of iodine appears to be predominately steric (see Part I, Chapter II), introduction of a second substituent iodine should have at least the same, and probably more of an effect than the first. Therefore, the rate of methoxide displacement of iodide ion from iodoform should be smaller than 3×10^{-8} l./m.s. (per mole of iodoform). Since the rate of reaction with hydroxide ion in aqueous dioxane should not be very different (at least it is not for chlorobromo- and dibromomethane, see references (1 and 2)), the S_N2 mechanism cannot be held responsible for the great reactivity of iodoform (at 50°C., 10^4k_h equal 7.2 l./m.s.).

(26) A. Butlerow, Ann., 114, 204 (1860). 118, 325 (1861).

(27) A. Garbow and A. Kessler, J. prakt. Chem., 41, 248 (1890).

Table 6. Kinetic Constants for the Basic Hydrolysis of Haloforms in Two-Thirds Aqueous Dioxane at 35°C.

Compound	$10^4 k_h$ (l./m.s.) Observed	Predicted
$CHCl_3$	3.01 ± 0.03	
$CHCl_2Br$	83.8 ± 1.2	
$CHClBr_2$	(35.5) [1] (1)	36.8
$CHBr_3$	12.1 ± 0.1	
$CHCl_2I$	39.9 ± 0.4 (1)	
$CHClI_2$	(1.78) [2]	5.38
CHI_3	(0.543) [2] (23)	

[1] Obtained by interpolation of values at zero, 25.3 and 35.7°C.

[2] Obtained by extrapolation from higher temperatures.

hydrolysis (compared to the rates in pure water) are plotted in Figure 2 as a function of the solvent composition. The numerical data are contained in Table 2. The reactivities of all the haloforms studied are increased by the presence of dioxane, the extent of the increase differing for the different haloforms. Those containing only chlorine and bromine as halogens are in no case accelerated by more than a factor of two over the range investigated.[1, 2]

[1] The presence of sodium hydroxide sets the upper limit at about 80 per cent dioxane by volume, above which salt solubilities are extremely limited.

[2] The effect upon chlorine, iodine containing haloforms seems to be somewhat greater. Dichloroiodomethane hydrolysis is accelerated 1.8 and 3.1 fold in 40 and 66 2/3 per cent dioxane, respectively (5).

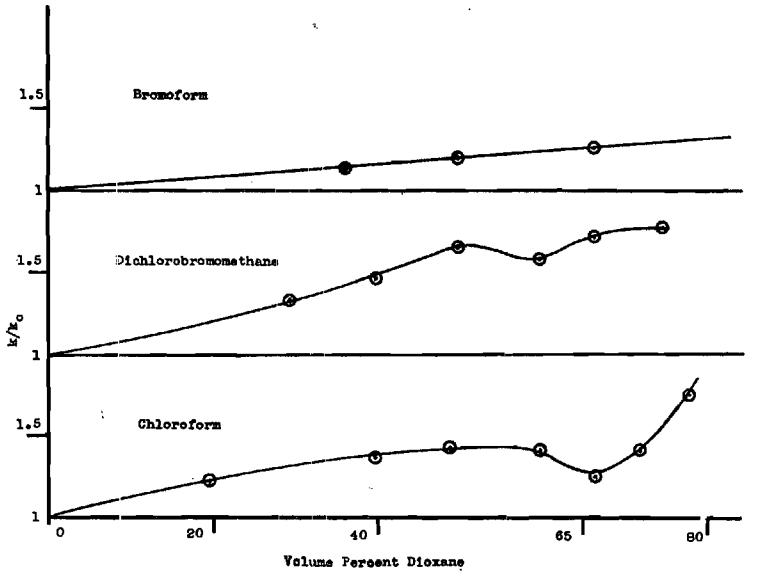


Fig. 2. The Relative Rates of Hydrolysis of Chloroform, Dichlorobromomethane and Bromoform versus Dioxane Concentration at 35°C.

The effects of varying the solvent composition appear quite complicated. For chloroform and dichlorobromomethane, distinct dips in the plots are apparent around 67 and 60 volume per cent dioxane, respectively, and for bromoform a similar situation, while not precisely definable from four points, is likely. The generally increased hydrolysis rate accompanying the introduction of dioxane is probably due to a compounding of effects upon the rate constants k_1, k_{-1}, and k_2, with the superimposed dips possibly resulting from ion pair formation between the sodium and trihalocarbanion and/or hydroxide ions. Martel and Kraus (28) have shown that several salts, including tetramethyl ammonium iodide and sodium bromate are considerably associated in aqueous dioxane solutions with

---

(28) R. W. Martel and C. A. Kraus, Proc. Nat. Acad. Sci., U. S., 41, 9 (1955).

dielectric constants below 50 (which corresponds to about 30 per cent dioxane by volume (29)). Without further experimental data a more precise analysis does not seem possible.

Methanolysis Reactions

The rates of methanolysis of the chlorine, bromine haloforms were measured at 50°C. in an attempt to test the applicability of the correlation method further. For chloroform, dichlorobromo- and chlorodibromomethane, the k_h values at 50°C. are, respectively, 0.306 ± 0.004, 9.25 ± 0.05 and 6.30 ± 0.07 l./m.s. Several runs were conducted with bromoform as the substrate with unsatisfactory results; the constants calculated by means of equation (2) dropped at first and then rose quite sharply. Reproducibility in neither the average nor the extrapolated values of the rate constants could be obtained between runs. The extrapolation to zero time of the log factor of equation (2) versus time exhibited considerable deviations from linearity.

While the inability to determine the rate constant of methanolysis for bromoform experimentally prevents an actual check upon the correlation method, assuming the applicability of the latter allows prediction of a value. Employing equation (15) and the data for the three haloforms above, a rate constant at 50°C. for bromoform equal to about 2×10^{-4} l./m.s. is obtained. This value is considerably below the range over

---

(29) F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, J. Am. Chem. Soc., 75, 1991 (1953).

which the experimentally determined constants varied (between 10 and 30 x 10^{-4} l./m.s.).[1]

Combining the facts that the bromoform hydrolysis reactions exhibit no noticeable rate constant irregularities in water and aqueous dioxane, that gross deviations in the rate constants calculated by means of equation (2) are noted, and that the range of the experimentally determined constants is considerably higher than the rate volume expected (only in methanol does bromoform appear to be more reactive than dichlorobromomethane), suggests the possibility that methanol and/or its conjugate base promote a competing side reaction. For example, perhaps bromoform is extremely sensitive to oxidation in methanol; small quantities of air unavoidably enter the reaction flask upon removal of aliquots even with the precautions taken. The method of following the reaction by taking single points from separate reaction vessels should test the oxidation premise. It seems reasonable, in conclusion, to recommend that further studies be initiated to determine whether or not side reactions do contribute and, if so, to uncover the methanolysis reaction and measure its rate.

General Conclusions

Of the 16 haloforms that are expected to undergo basic solvolysis by the alpha elimination mechanism, ten have been studied in water and

---

[1]The S_N2 reactivity of bromoform toward methoxide in methanol may be estimated in a manner similar to that employed for iodoform (see page 99, footnote 2). Replacing one hydrogen by bromine in methyl bromide decreases the reactivity toward methoxide by about 650 fold at 50°C. (10^5k, from 472 to 0.74 l./m.s. (2). The rate constant for methoxide displacement of bromide ion from bromoform, therefore, should be less than 2 x 10^{-8} l./m.s. (per mole of bromoform).

found to be amenable at a reaction temperature of zero degrees to fitting by a semi-empirical correlation equation with six parameters. Sufficient data have been collected to indicate that a similar correlation is successful in two-thirds aqueous dioxane for chlorine, bromine containing haloforms. While the chlorine, iodine haloforms do not seem adaptable to the method in this solvent, further investigation, especially of the iodoform reaction, appears necessary before this group establishes a class of exceptions to the correlation. The methanolysis reactions have been insufficiently examined to constitute either support or detraction from the correlation method.

It may be ventured that the studies carried out on the hydrolysis reactions in water and, to some degree, in aqueous dioxane, and the subsequent mathematical manipulations of the resulting data have, besides strengthening support for the alpha elimination mechanism and allowing prediction of the reactivities of the other six haloforms, provided a means of separating the factors contributing to the overall measurable hydrolysis rates. When further studies on several or all the remaining haloforms are completed and the most likely values for the parameters calculated, evaluation of the contributions of such factors as trihalocarbanion and dihalomethylene stabilization may be accomplished within the limits imposed by the correlation methods' assumptions.

CHAPTER V

RECOMMENDATIONS

Renewed study of the hydrolysis reaction of iodoform in two-thirds dioxane and of the methanolysis of bromoform are of primary interest. Extension of the investigations in these solvents to include various other haloforms, notably those containing fluorine, is also suggested. Knowledge of the values of k_1 might be obtained directly by use of a tritium tracer technique in wholly, or mixed aqueous, organic solvents.[1]

Examination of all or some of the six haloforms not as yet studied in water would be useful in order to test the correlation further. Especially of interest are the bromine, iodine containing haloforms, which, according to equation (10) and the pertinent parameters, should form dihalomethylenes both from loss of bromide and iodide ions. Of course, a study of iodoform in pure aqueous solution is called for in light of the discrepancy suspected for this compound in aqueous dioxane. Such a study may be difficult to execute at any temperature below 50°C., noting the extremely slow rate of hydrolysis predicted by equation (10). The extrapolation to zero degrees from such distant temperatures would be of limited value.

This point brings another recommendation to the fore. It would certainly be of value to apply the correlation method at one, or more,

---

[1] For example, label the haloform and during the reaction remove aliquots of the reaction solution, extract some of the haloform from the solvent and measure its radioactivity. The advantage of this technique lies in the possibility of measurement of exchange from very small quantities of extracted haloform.

additional temperatures. A successful fit at another temperature would support its credibility.

APPENDIX

TABLES

Table 7. $CHCl_3$ + NaOH in 78 Per Cent[1] Aqueous Dioxane at 35°C.

$CHCl_3$ 0.01100 M — HCl 0.0386 M

NaOH 0.01468 M — 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	7.59	---
258	6.15	4.140
404	5.48	4.166
872	3.80	4.367
897	3.78	4.282
1093	3.35	4.192
1254	3.02	4.184
1721	2.25	4.177
2505	1.33	4.374

[1]Corrected values for solvent composition, see page 72.

f = 0.15, k = (4.235 ± 0.081) x 10^{-4} l./m.s.

Table 8. $CHCl_3$ + NaOH in 18 Per Cent[1] Aqueous Dioxane at 35°C.

$CHCl_3$ 0.01222 M — HCl 0.0386 M

NaOH 0.01123 M — 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	5.82	---
423	4.37	3.054
596	3.95	2.968
982	3.10	3.062
1139	2.84	2.983
1274	2.63	2.972
1455	2.41	2.918
1873	1.84	3.033

[1]Corrected value for solvent composition, see page 72.

f = 0.15, k = (2.999 ± 0.044) x 10^{-4} l./m.s.

Table 9. $CHCl_3$ + NaOH in 48 Per Cent[1] Aqueous Dioxane at 35°C.

$CHCl_3$ 0.01222 M HCl 0.0386 M

NaOH 0.01123 M 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	5.82	---
426	4.14	3.624
595	3.72	3.455
982	2.83	3.479
1139	2.52	3.525
1273	2.36	3.415
1454	2.11	3.403
1880	1.60	3.424

[1]Corrected value for solvent composition, see page 72.

f = 0.15, k = (3.475 ± 0.054) x 10^{-4} l./m.s.

Table 10. $CHCl_3$ + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 35°C.

$CHCl_3$ 0.02572 M HCl 0.0386 M

NaOH 0.03995 M 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	20.70	---
114	17.62	3.025
172	16.34	2.996
276	14.31	3.001
307	13.69	3.051
478	11.31	2.983
695	9.00	2.957
1155	5.61	3.023
1346	4.72	3.021

f = 0.15, k = (3.007 ± 0.024) x 10^{-4} l./m.s.

Table 11. $CHCl_3$ + NaOH in 72 Per Cent Aqueous Dioxane at 35°C.

$CHCl_3$ 0.01104 M HCl 0.0386 M

NaOH 0.02727 M 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	14.13	---
442	10.58	3.515
542	10.11	3.379
645	9.43	3.520
948	8.13	3.463
1084	7.74	3.360
1277	7.10	3.371
1467	6.49	3.426
2049	5.16	3.453
2425	4.45	3.525

f = 0.15, k= (3.446 ± 0.055) x 10^{-4} l./m.s.

Table 12. $CHCl_3$ + NaOH in 60 Per Cent Aqueous Dioxane at 35°C.

$CHCl_3$ 0.02959 M HCl 0.0386 M

NaOH 0.01666 M 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	8.63	---
78	7.43	3.420
194	6.03	3.404
230	5.58	3.513
365	4.35	3.533
433	3.97	3.398
1025	1.58	3.273

f = 0.15, k = (3.423 ± 0.066) x 10^{-4} l./m.s.

Table 13. $CHCl_2Br$ + NaOH in 60 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.008536 M HCl 0.0386 M

NaOH 0.03682 M 10 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	9.54	---
660	8.41	77.70
1410	7.49	76.19
2130	6.83	75.02
3330	5.97	75.62
4455	5.32	78.43
5790	4.81	78.61
7125	4.49	76.05

f = 0.15, k = (76.80 ± 1.08) x 10^{-4} l./m.s.

Table 14. $CHCl_2Br$ + NaOH in 50 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.008300 M HCl 0.0386 M

NaOH 0.03717 M 10 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	9.63	---
945	8.10	79.52
1875	7.09	79.15
2730	6.40	79.51
3795	5.73	80.80
5175	5.15	80.06
7485	4.42	83.26
8400	4.25	82.29

f = 0.15, k = (80.66 ± 1.29) x 10^{-4} l./m.s.

Table 15. $CHCl_2Br$ + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.008422 M HCl 0.0386 M

NaOH 0.04196 M 10 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	10.87	---
1170	8.76	83.71
1635	8.21	82.82
2415	7.49	81.76
3465	6.71	83.68
4890	6.04	83.00
6825	5.36	86.53
8745	5.00	85.13

f = 0.15, k = (83.80 ± 1.17) x 10^{-4} l./m.s.

Table 16. $CHCl_2Br$ + NaOH in 29.4 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.008725 M HCl 0.04128 M

NaOH 0.01587 M 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	7.69	---
930	6.57	64.34
1470	6.03	64.33
2070	5.49	65.06
2745	4.95	65.85
3240	4.60	66.46
4095	4.09	66.51
5160	3.58	65.97
5970	3.23	66.24
7470	2.70	66.56
8565	2.44	64.96

f = 0.15, k = (65.63 ± 0.79) x 10^{-4} l./m.s.

Table 17. $CHCl_2Br$ + NaOH in 40 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.009435 M HCl 0.0386 M

NaOH 0.04219 M 10 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 l./m.s.
0	10.93	---
885	9.26	71.35
1575	8.34	71.11
2415	7.49	71.11
3450	6.73	70.56
4950	5.88	72.37
8625	4.90	67.58
10305	4.53	69.88

f = 0.15, k = (70.56 ± 1.06) x 10^{-4} l./m.s.

Table 18. $CHCl_2Br$ + NaOH in 75 Per Cent Aqueous Dioxane at 35°C.

$CHCl_2Br$ 0.015606 M HCl 0.04128

NaOH 0.02033 M 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	9.85	---
780	7.22	86.66
1200	6.21	85.60
1575	5.41	86.65
2010	4.69	86.03
2415	4.08	86.83
2835	3.66	84.41
3300	3.10	86.49
3765	2.73	85.44

f = 0.15, k = (86.01 ± 0.65) x 10^{-4} l./m.s.

Table 19. $CHBr_3$ + NaOH in 36.4 Per Cent Aqueous Dioxane at 35°C.

$CHBr_3$ 0.01620 M HCl 0.04128 M

NaOH 0.01957 M 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	9.48	---
3705	7.79	11.02
5490	7.11	11.05
9120	5.95	11.14
12255	5.16	11.07
13860	4.80	11.07
16635	4.33	10.78

f = 0.08, k = (11.02 ± 0.08) x 10^{-4} l./m.s.

Table 20. $CHBr_3$ + NaOH in 50 Per Cent Aqueous Dioxane at 35°C.

$CHBr_3$ 0.01264 M HCl 0.04128 M

NaOH 0.02105 M 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	10.20	---
1215	9.65	11.85
3420	8.78	11.72
4830	8.30	11.58
6960	7.62	11.61
9255	7.00	11.51
10875	6.59	11.55
14220	5.77	11.88
16695	5.41	11.43
27105	3.92	11.39

f = 0.08, k = (11.61 ± 0.14) x 10^{-4} l./m.s.

Table 21. $CHBr_3$ + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 35°C.

$CHBr_3$ 0.009398 M — HCl 0.04128 M

NaOH 0.01992 M — 20 ml. samples

Time in Seconds	ml. of HCl	$k \times 10^4$ (l./m.s.)
0	9.65	---
5055	8.18	11.98
6975	7.69	12.16
8955	7.27	12.05
12165	6.64	12.03
14325	6.27	12.03
19185	5.52	12.12
23550	4.94	12.24

$f = 0.08$, $k = (12.09 \pm 0.06) \times 10^{-4}$ l./m.s.

Table 22. $CHClI_2$ + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 50°C.

$CHClI_2$ 0.008643 M — $HClO_4$ 0.04093 M

NaOH 0.01580 M — 25 ml. samples

Time in Seconds	ml. of HCl	$k \times 10^4$ (l./m.s.)
0	9.65	---
1730	8.91	18.16
3705	8.19	17.92
6590	7.34	17.35
11310	6.17	17.39
14520	5.52	17.43
18310	4.77	18.13

$f = 0.00$, $k = (17.74 \pm 0.34) \times 10^{-4}$ l./m.s.

Table 23. $CHClI_2$ + NaOH in 66 2/3 Per Cent Aqueous Dioxane at 67.1°C.

$CHClI_2$ 0.01031 M — $HClO_4$ 0.04093 M

NaOH 0.01400 M — 25 ml. samples

Time in Seconds	ml. of $HClO_4$	k x 10^4 (l./m.s.)
0	8.55	---
95	8.19	---
195	7.82	---
605	6.06	198.2
1085	4.83	191.4
1385	4.23	189.2
2015	3.34	180.9
2525	2.72	181.7
2885	2.32	185.0

f = 0.00, k = (187.8 ± 5.2) x 10^{-4} l./m.s.

Graphically, k = (179 ± 9) x 10^{-4} l./m.s., see page

Table 24. $CHCl_3$ + $NaOCH_3$ in Absolute Methanol at 50°C.

$CHCl_3$ 0.01461 M — HCl 0.04128 M

$NaOCH_3$ 0.02235 M — 20 ml. samples

Time in Minutes	ml. of HCl	k x 10^4 (l./m.s.)
0	10.83	---
887	10.08	0.3110
1560	9.56	0.3133
2255	9.10	0.3063
3616	8.25	0.3056
5193	7.47	0.2975
5953	7.09	0.2995

f = 0.00, k = (0.3056 ± 0.0047) x 10^{-4} l./m.s.

Table 25. $CHCl_2Br$ + $NaOCH_3$ in Absolute Methanol at 50°C.

$CHCl_2Br$ 0.01436 M — HCl 0.04128 M

$NaOCH_3$ 0.02758 M — 15 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	10.02	---
4560	8.46	9.118
6195	7.97	9.234
8340	7.40	9.273
13080	6.34	9.359
15030	6.01	9.242
18375	5.46	9.224
24390	4.61	9.318
30510	3.95	9.311
75060	1.58	9.216

f = 0.00, k = (9.253 ± 0.046) x 10^{-4} l./m.s.

Table 26. $CHClBr_2$ + $NaOCH_3$ in Absolute Methanol at 50°C.

$CHClBr_2$ 0.01472 M — HCl 0.04128 M

$NaOCH_3$ 0.02931 M — 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	14.20	---
5760	12.19	6.315
7755	11.54	6.485
11535	10.63	6.250
14730	9.89	6.257
20460	8.72	6.309
25275	8.01	6.157

f = 0.00, k = (6.295 ± 0.074) x 10^{-4} l./m.s.

Table 27. $CHCl_2Br$ + NaOH in Water at 50°C.

$CHCl_2Br$ 0.007268 M — HCl 0.04128 M

NaOH 0.01402 M — 20 ml. samples

Time in Seconds	ml. of HCl	k x 10^4 (l./m.s.)
0	6.79	---
68	6.52	---
142	6.24	---
545	4.88	292.8
812	4.16	304.4
945	3.86	307.7
1155	3.49	305.3
1375	3.23	291.6
1700	2.89	278.8
2215	2.50	259.6
2692	2.21	247.1
2930	2.11	258.7

f = 0.15, Average k = (282.9 ± 19.4) x 10^{-4} l./m.s.

Graphically, k = (307 ± 24) x 10^{-4} l./m.s., see page

Table 28. $CHBr_3$ + NaOH in Water at 25°C.

$CHBr_3$ 0.01198 M — $HClO_4$ 0.04093 M

NaOH 0.01617 M — 20 ml. samples

Time in Minutes	ml. of $HClO_4$	k x 10^4 (l./m.s.)
0	7.90	---
662	5.99	2.002
891	5.45	2.035
1160	4.95	2.003
1380	4.56	2.010
2124	3.57	1.967
2815	2.88	1.953
3582	2.30	1.935

f = 0.08, k = (1.986 ± 0.030) x 10^{-4} l./m.s.

Table 29. $CHBr_3$ + NaOH in Water at 35°C.

$CHBr_3$ (a) 0.01371 M
(b) 0.008420 M

NaOH (a) 0.02103 M
(b) 0.02418 M

(a) HCl 0.04128 M

(b) $HClO_4$ 0.07522 M

20 ml. samples

Time in Seconds		ml. of HCl	k x 10^4 (l./m.s.)
(a)	0	10.10	---
(b)	0	6.43	---
(a)	1725	9.51	9.263
	4785	8.44	9.762
	6645	7.90	9.635
	9570	7.14	9.573
(b)	9585	5.19	9.518
(a)	11280	6.66	9.860
	13995	6.14	9.648
(b)	24030	4.04	9.305
	42585	3.11	9.347
(a)	52455	2.15	9.504

f = 0.08, k = (9.542 ± 0.144) x 10^{-4} l./m.s.

Table 30. $CHBr_3$ + NaOH in Water at 50°C.

$CHBr_3$ 0.01427 M

NaOH 0.01801 M

$HClO_4$ 0.04093 M

20 ml. samples

Time in Seconds	ml. of $HClO_4$	k x 10^4 (l./m.s.)
0	8.80	---
145	8.30	---
280	7.86	---
540	7.14	91.89
920	6.25	90.45
1385	5.37	89.04
1875	4.54	91.11
2275	4.13	86.67
2595	3.78	85.92
3160	3.25	85.06
3695	2.89	82.65
4315	2.49	81.65
4820	2.21	81.23

f = 0.08, Average k = (86.57 ± 3.37) x 10^{-4} l./m.s.

Graphically, k = (83.8 ± 3.4) x 10^{-4} l./m.s., see page

Table 31. $CHCl_2I$ + NaOH in Water at 25°C.

$CHCl_2I$ 0.01299 M — $HClO_4$ 0.04093 M

NaOH 0.01783 M — 20 ml. samples

Time in Minutes	ml. of $HClO_4$	k x 10^4 (l./m.s.)
0	8.71	---
265	7.56	2.248
428	7.00	2.177
1175	5.01	2.143
1328	4.66	2.169
1848	3.84	2.109
2496	2.96	2.141

f = 0.015, k = (2.165 ± 0.030) x 10^{-4} l./m.s.

Table 32. $CHCl_2I$ + NaOH in Water at 50°C.

$CHCl_2I$ 0.009374 M — $HClO_4$ 0.04093 M

NaOH 0.01719 M — 20 ml. samples

Time in Seconds	ml. of $HClO_4$	k x 10^4 (l./m.s.)
0	8.40	---
190	7.95	---
440	7.39	---
795	6.63	107.7
1145	6.05	106.5
1510	5.54	104.8
2030	4.92	103.3
2170	4.81	101.5
2585	4.41	100.4
3135	4.02	96.93
3710	3.69	93.41
4425	3.22	94.17

f = 0.15, Average k = (101.0 ± 4.2) x 10^{-4} l./m.s.

Graphically, k = (95.2 ± 5.8) x 10^{-4} l./m.s.

Table 33. $CHClI_2$ + NaOH in Water at 50°C.

$CHClI_2$	(a)	0.002024 M	NaOH	(a)	0.005332 M
	(b)	0.001856 M		(b)	0.004966 M
	(c)	0.003092 M		(c)	0.006140 M
$HClO_4$		0.04093 M	(a) and (b)		75 ml. samples
$AgNO_3$		0.0596 M	(c)		40 ml. samples

	Time in Minutes	ml. of $HClO_4$	ml. of $AgNO_3$ (f)		k x 10^4 (l./m.s.)
(a)	0	9.77			---
(b)	0	9.10			---
(c)	0	6.00			---
(a)	125	9.38			9.046
(c)	261	5.23	0.52	(.05)	9.890
(a)	454	8.44			9.426
(b)	685	7.51			9.163
(c)	892	4.13	1.33	(-.10)	8.493
(c)	1363	3.37	1.93	(-.19)	9.134
(b)	1516	5.79			10.96 [1]
(c)	1611	3.05	2.14	(-.16)	9.335

[1] Not Averaged.

f = 0.00, k = (9.212 ± 0.290) x 10^{-4} l./m.s.

Table 34. $CHClI_2$ + NaOH in Water at 67.1°C.

$CHClI_2$ (a) 0.003848 M
(b) 0.004063 M

NaOH (a) 0.004779 M
(b) 0.004922 M

$HClO_4$ 0.04093 M

40 ml. samples

Time in Seconds		ml. of $HClO_4$	k x 10^4 (l./m.s.)
(a)	0	4.67	---
(b)	0	4.81	---
(b)	77	4.71	---
(a)	88	4.56	---
(a)	217	4.40	---
(b)	232	4.52	---
(a)	514	4.24	165.9
(b)	820	4.16	149.6
(a)	890	4.06	140.3
(b)	1265	3.90	141.7
(a)	1668	3.69	128.2
(b)	1835	3.62	134.3
(a)	2675	3.37	112.9
(b)	3290	3.09	119.9

f = 0.00, Average k = (136.6 ± 12.8) x 10^{-4} l./m.s.

Graphically, k = (112 ± 25) x 10^{-4} l./m.s.

Table 35. $CHBr_3$ + NaOH in Water at 35°C.

Determination of f

$CHBr_3$ 0.008420 M

NaOH 0.02419 M

$AgNO_3$ 0.0483 M

$HClO_4$ 0.07522 M

(a) 20 ml. samples
(b) 50 ml. samples

Time in Minutes		ml. of $HClO_4$	ml. of $AgNO_3$	(f)
(b)[1]	0	16.08 [1]	---	---
(a)	3.25	6.40	---	---
(a)	5.25	6.38	---	---
(b)	159.75	12.98	5.05	-0.13
(b)	400.50	10.10	9.31	0.00
(b)	709.75	7.77	12.67	0.06
(b)	1347.50	5.38	16.50	0.03

[1] Extrapolated value assuming 50 ml. samples.

BIBLIOGRAPHY

Literature Cited

(1) Hine, J., A. M. Dowell, Jr., and J. E. Singley, Jr., Journal of the American Chemical Society, 78, 479 (1956).

(2) Hine, J., C. H. Thomas, and S. J. Ehrenson, ibid., 77, 3886 (1955).

(3) Hine, J., ibid., 72, 2438 (1950).

(4) Hine, J., Unpublished work.

(5) Dowell, A. M., Jr., The Mechanism of the Basic Hydrolysis of Haloforms, Unpublished Ph.D. Thesis, Georgia Institute of Technology, 1954.

(6) Tommila, E., and A. Koivisto, Suomen Kemistelehti, 21B, 18 (1948). Chemical Abstracts, 42, 8059d (1948).

(7) Bates, R. G., and G. Schwarzenbach, Helvetica Chimica Acta, 37, 1069 (1954).

(8) Handbook of Chemistry and Physics, 30th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1947, p. 1402.

(9) Treadwell, W. D., and G. Schwarzenbach, Helvetica Chimica Acta, 11, 386 (1928).

(10) Benkeser, R. A., and H. R. Krysiak, Journal of the American Chemical Society, 75, 2421 (1953).

(11) Kolthoff, I. M., and L. S. Guss, ibid., 60, 2516 (1938).

(12) Fieser, L. F., Experiments in Organic Chemistry, Part II, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(13) Auger, V., Comptes rendus hebdomadaires des séances de l'académie des sciences, 146, 1037 (1908).

(14) Singley, J. E., Jr., Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms, Unpublished M.S. Thesis, Georgia Institute of Technology, 1952.

(15) Leimu, R., Berichte der deutschen chemischen Gesellschaft, 70B, 1040 (1937).

(16) Karrer, P., Organic Chemistry, Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 228.

(17) Hine, J., and N. W. Burske, Journal of the American Chemical Society, 78, 3337 (1956).

(18) Hine, J., N. W. Burske, M. Hine, and P. B. Langford, ibid., In press.

(19) Hine, J., and A. M. Dowell, Jr., ibid., 76, 2688 (1954).

(20) Pearson, R. G., and R. L. Dillon, ibid., 75, 2439 (1953).

(21) Hine, J., R. C. Peek, Jr., and B. D. Oakes, ibid., 76, 827 (1954).

(22) Peek, R. C., Jr., Unpublished data from a single point.

(23) Hine, J., and P. B. Langford, Unpublished work.

(24) Butterworth, R., The Mechanism of the Basic Hydrolysis of Dibromochloromethane and Dibromofluoromethane, Part I, Unpublished M.S. Thesis, Georgia Institute of Technology, 1956.

(25) Streitwieser, A., Jr., Chemical Reviews, 56, 654 (1956).

(26) Boutlerow, A., Justus Liebigs Annalen der Chemie, 114, 204 (1860). 118, 325 (1861).

(27) Garbow, A., and A. Kessler, Journal für praktische Chemie, 41, 248 (1890).

(28) Martel, R. W., and C. A. Kraus, Proceedings of the National Academy of Sciences of the United States of America, 41, 9 (1955).

(29) Critchfield, F. E., J. A. Gibson, Jr., and J. L. Hall, Journal of the American Chemical Society, 75, 1991 (1953).

VITA

Stanton Jay Ehrenson was born on October 13, 1931 in New York City, the son of Miriam (nee Stein) and Alexander Ehrenson. After three years spent in Long Beach, New York, residence was established in the borough of The Bronx where he attended public primary and secondary schools. He entered Long Island University in September of 1949 and obtained the Bachelor of Science degree in Chemistry in June of 1952. The opening of the following school year found him at the University of Wisconsin where he taught and did research until January of 1954, having taken the Master of Science degree in Chemistry. He entered the Georgia Institute of Technology the following month, recipient of a research fellowship under a grant from the National Science Foundation. Grants from the Tennessee Eastman Corporation and the Office of Ordnance Research also supported his work until February of 1957. He has accepted a postdoctoral fellowship for one year at the Pennsylvania State University.